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MANUAL OF

QUALITATIVE CHEMICAL

ANALYSIS.

BY

DR. C. REMIGIUS FRESENIUS.

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From the last English and German Editions.

EDITED BY

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EDITOR'S PREFACE.

NOTWITHSTANDING the rapid multiplication of Treatises on Qualitative Chemical Analysis, the Manual of Fresenius maintains a well deserved popularity. Though apparently somewhat complicated in its arrangement, it is in use incomparably the most trustworthy guide the chemist can employ.

The present contains all the improvements of the eleventh German and sixth English editions. The editor has employed as its basis the text of the fifth London issue, and has incorporated with it his own translation of the corrections and new matter of the last German edition; the Appendix alone excepted, which is reprinted from the sixth English edition, just published.

The matter newly added to this work by the author relates chiefly to the RARER ELEMENTS, to FLAME-TESTS, SPECTRAL ANALYSIS, DIALYSIS, and the REACTIONS OF THE ALKALOIDS. The course of Analysis has also received some important modifications. The editor has added a few notes which are distinguished by inclosure in brackets [ ]. In one or two instances he has substituted his own matter for that of the author, and he has omitted altogether a few unimportant paragraphs.

The colored spectrum-plate of the foreign editions, which is not only incomplete but erroneous, has been replaced in this work by the more recent and useful plain plate of *Kirchhof* and *Bunsen*.

SAMUEL W. JOHNSON,
Sheffield Laboratory of Yale College.

May, 1864.

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PART I.

INTRODUCTORY.

PRELIMINARY REMARKS.

DEFINITION, GENERAL PRINCIPLES, OBJECTS, UTILITY, AND IMPORTANCE OF QUALITATIVE CHEMICAL ANALYSIS, THE CONDITIONS AND REQUIREMENTS FOR A SUCCESSFUL STUDY OF THAT SCIENCE.

CHEMISTRY is the science which treats of the various materials entering into the structure of the earth, their composition and decomposition, their mutual relations and deportment in general. A special branch of this science is designated *Analytical Chemistry*, inasmuch as it pursues a distinct and definite object—viz., the analysis of compound bodies, and the examination of their component elements. Analytical chemistry, again, is subdivided into two branches—viz., *qualitative analysis*, which simply studies the *nature* and properties of the component parts of bodies; and *quantitative analysis*, which ascertains the *quantity* of every individual element present. The office of qualitative analysis, therefore, is to exhibit the constituent parts of a substance of *unknown* composition in forms of *known* composition, from which the constitution of the body examined, and the presence of its several component elements may be positively inferred. The efficiency of its method depends upon two conditions—viz., it must attain the object in view with unerring certainty, and in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation in forms which will permit the most accurate estimate of their weight, or to effect by other means the determination of their quantity.

These different ends are, of course, attained respectively by very different ways and means. The study of qualitative analysis must, therefore, be pursued separately from that of quantitative analysis, and must naturally precede it.

Having thus generally defined the meaning and scope of qualita-

tive analysis, we have now still to consider, in the first place, the preliminary information required to qualify students for a successful cultivation of this branch of science, the rank which it holds in the domain of chemistry, the bodies that fall within the sphere of its operations, and its utility and importance; and, in the second place, the principal parts into which its study is divided.

It is, above all, absolutely indispensable for a successful pursuit of qualitative investigations, that the student should possess some knowledge of the chemical *elements*, and of their most important combinations, as well as of the principles of chemistry in general; and that he should combine with this knowledge some readiness in the apprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student joins to these qualifications the habit of invariably ascribing the failures with which he may happen to meet, to some error or defect in his operations, or, in other words, to the absence of some condition or other indispensable to the success of the experiment—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit—he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we have to look upon it as one of the main pillars upon which the entire structure of the science rests; since it is of almost equal importance for all branches of theoretical as well as of practical chemistry; and I need not expatiate here on the advantages which the physician, the pharmaceutist, the mineralogist, the rational farmer, the manufacturer, the artisan, and many others derive from it.

This consideration would surely in itself be sufficient reason to recommend a thorough and diligent study of this branch of science, even if its cultivation lacked those attractions which yet it unquestionably possesses for every one who devotes himself zealously and ardently to it. The human mind is constantly striving for the attainment of truth; it delights in the solution of problems; and where do we meet with a greater variety of them, more or less difficult of solution, than in the province of chemistry? but as a problem to which, after long pondering, we fail to discover the key, wearies and discourages the mind: so, in like manner, do chemical investigations, if the object in view is not attained—if the results do not bear the stamp of truth, of unerring certainty. A *half-knowledge* is therefore, as indeed in every department of science, but more especially *here*, to be considered worse than no knowledge at all; and a mere *superficial* cultivation of chemical analysis is consequently to be particularly guarded against.

A qualitative investigation may be made with a twofold view—viz., either, 1st, to prove that a certain body is or is not contained in a substance, *e.g.* lead in wine; or, 2nd, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may of course become the object of a chemical analysis.

In this work, those bodies which are most important in practical chemistry, from their wide distribution and their uses in medicine and the arts, are treated of in full detail; while, to facilitate the beginner's progress, the rarer elements are noticed more briefly, and in such a manner that they may be separately studied.

The study of qualitative analysis is most properly divided into four principal parts—viz.,

1. Chemical operations.
2. Reagents and their uses.
3. Deportment of the various bodies with reagents.
4. Systematic course of qualitative analysis.

It will now be readily understood that the pursuit of chemical analysis requires *practical skill and ability*, as well as *theoretical knowledge;* and that, consequently, a mere speculative study of that science can be as little expected to lead to success as purely empirical experiments. To attain the desired end, theory and practice must be combined.

SECTION I.

OPERATIONS.

§ 1.

The operations of analytical chemistry are essentially the same as those of synthetical chemistry, though modified to a certain extent to adapt them to the different object in view, and to the small quantities operated upon in analytical investigations.

The following are the principal operations in qualitative analysis.

§ 2.

1. Solution.

The term "*solution*," in its widest sense, denotes the perfect union of a body, no matter whether gaseous, liquid, or solid, with a fluid, resulting in a homogeneous liquid. However, when the substance dissolved is *gaseous*, the term "*absorption*" is more properly made use of; and the solution of one fluid in another is more generally called a *mixture*. The application of the term

solution, in its usual and more restricted sense, is confined to the perfect union of a *solid* body with a fluid.

A solution is the more readily effected the more minutely the body to be dissolved is divided. The fluid by means of which the solution is effected, is called the *solvent.* We call the solution *chemical*, where the solvent enters into chemical combination with the substance dissolved; *simple*, where no definite combination takes place.

In a *simple* solution the dissolved body exists in the free state, and retains all its original properties, except those dependent on its form and cohesion; it separates unaltered when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the fluid. On evaporating the water, the salt is left behind in its original form. A simple solution is called *saturated* when the solvent has received as much as it can hold of the dissolved substance. But as fluids dissolve generally larger quantities of a substance, the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. It may be laid down as a general rule, that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, which latter also has lost its original properties; a new substance has thus been produced, and the solution manifests therefore now the properties of this new substance. A chemical solution also may be *accelerated* by elevation of temperature; and this is indeed usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference of temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature.

The reason of this is, that in a chemical solution the solvent and the body upon which it acts have invariably opposite properties, which they strive mutually to neutralize. Further solution ceases as soon as this tendency of mutual neutralization is satisfied. The solution is in this case also said to be saturated, or, more properly, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization.

The substances which produce chemical solutions are, in most cases, either acids or alkalies. With few exceptions, they have first to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neu-

tralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present; *e. g.* when solution of acetic acid in water is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and then a simple solution of the new-formed acetate of lead in the water of the menstruum.

In pharmacy, solutions are often made in a mortar by triturating the body to be dissolved with the solvent added gradually in small quantities at a time; in chemical laboratories solutions are rarely made in this manner, but generally by digesting or heating the substance to be dissolved with the fluid in beaker-glasses, flasks, test-tubes, or capsules. In the preparation of chemical solutions, the best way generally is to mix the body to be dissolved in the first place with water (or with whatever other indifferent fluid may happen to be used), and then gradually add the chemical agent. By this course of proceeding a large excess of the latter is avoided, an over-energetic action guarded against, the process greatly facilitated, and complete solution ensured, which is a matter of some importance, as it will not seldom happen in chemical combinations that the product formed refuses to dissolve if an excess of the chemical solvent is present; in which case the molecules first formed of the new salt, being insoluble in the menstruum present, gather round and enclose the portion still unacted on, weakening thereby or preventing altogether further chemical action upon them. Thus, for instance, Witherite (carbonate of baryta) dissolves readily when, after being reduced to powder, water is poured upon it, and hydrochloric acid gradually added; but it dissolves with difficulty and imperfectly when projected into a concentrated solution of hydrochloric aid in water, for chloride of barium will indeed dissolve in water, but not in hydrochloric acid.

CRYSTALLIZATION and PRECIPITATION are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both generally depend on the same cause, viz., on the absence of a solvent, it is impossible to assign exact limits to either; in many cases they merge into one another. We must, however, consider them separately here, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

§ 3.

2. Crystallization.

We understand by the term crystallization, in a more general sense, every operation, or process, whereby bodies are made to pass from the fluid to the solid state, and to assume certain fixed, mathematically definable, regular forms. But as these forms, which we call *crystals*, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term "crystallization" the accessory idea of a *slow* separation—of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate constituent particles of bodies (*molecules* or *atoms*); it can only take place, therefore, if these atoms possess perfect freedom of motion, and thus in general only when a substance passes from the fluid or gaseous to the solid state. Those instances in which the mere ignition, or the softening or moistening of a solid body, suffices to make the tendency of the molecules to a regular arrangement (crystallization) prevail over the diminished force of cohesion—such as, for instance, the turning white and opaque of moistened barley-sugar—are to be regarded as exceptional cases.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat alone*, *e. g.*, in the case of fused metals; or *solvents alone*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of nitrate of potassa in water. In the first case we obtain crystals by cooling the fused mass; in the second, by evaporating the menstruum; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquors which remain after the separation of the crystals are called *mother-waters*, or *mother-liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We have recourse to crystallization generally either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same menstruum. In many cases also the form of the crystals or their deportment in the air, viz., whether they remain unaltered or effloresce, or deliquesce, upon exposure to the air, will afford an excellent means of distinguishing between bodies otherwise resembling each other; for instance, between sulphate of soda and sulphate of potassa. The process of crystallization is usually effected in dishes, or, in the case of very small quantities, in watch-glasses.

In cases where the quantity of fluid to be operated upon is small,

the surest way of getting well-formed crystals is to let the fluid evaporate in the air, or, better still, under a bell-glass, with an open vessel half-filled with concentrated sulphuric acid. Minute crystals are examined best with a lens, or under the microscope.

§ 4.

3. Precipitation.

This operation differs from the preceding one in this much, that the dissolved body is converted to the solid state, not slowly and gradually, but *suddenly*, no matter whether the substance separating is crystalline or amorphous, whether it sinks to the bottom of the vessel, or ascends, or remains suspended in the liquid. Precipitation is either caused by a modification of the solvent—thus sulphate of lime (gypsum) separates immediately from its solution in water upon the addition of alcohol; or it ensues in consequence of the separation of an educt insoluble in the menstruum—thus when ammonia is added to a solution of sulphate of alumina, the latter salt is decomposed, and the alumina, not being soluble in water, precipitates. Precipitation takes place also when, by the action of simple or double chemical affinity, new compounds are formed which are insoluble in the menstruum; thus oxalate of lime precipitates upon adding oxalic acid to a solution of acetate of lime; chromate of lead upon mixing chromate of potassa with nitrate of lead. In decompositions of this kind, induced by simple or double affinity, one of the new compounds remains generally in solution, and the same is sometimes the case also with the educt; thus in the instances just mentioned the sulphate of ammonia, the acetic acid, and the nitrate of potassa, remain in solution. It may, however, happen also that both the product and the educt, or two products, precipitate, and that nothing remains in solution; this is the case, for instance, when a solution of sulphate of magnesia is mixed with water of baryta, or when a solution of sulphate of silver is precipitated with chloride of barium.

Precipitation is resorted to for the same purposes as crystallization, viz., either to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we have recourse to this operation more particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process is called the *precipitate*, and the substance which acts as the immediate cause of the separation is termed the *precipitant*. Various terms are applied to precipitates by way of particularizing

them according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, &c.

The terms *turbid*, *turbidity*, are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally be promoted by a vigorous shake of the vessel; that of crystalline precipitates, by stirring the fluid and rubbing the sides of the vessel with a glass rod; elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is therefore conducted, according to circumstances, either in test-tubes, flasks, or beakers.

The two operations described respectively in §§ 5 and 6, viz., *filtration* and *decantation*, serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. Filtration.

This operation consists simply in passing the fluid from which we wish to remove the solid particles mechanically suspended therein through a filtering apparatus, formed usually by a properly arranged piece of unsized paper placed in a funnel; an apparatus of this description allows the fluid to trickle through with ease, whilst it completely retains the solid particles. We employ smooth filters and plaited filters; the former in cases where the separated solid substance is to be made use of, the latter in cases where it is simply intended to clear the solution. Smooth filters are prepared by double-folding a circular piece of paper, with the folds at right angles; they must in every part fit close to the funnel. The preparation of plaited filters is more properly a matter for ocular demonstration than for description. In cases where the contents of the filter require washing, the paper must not project over the rim of the funnel. It is in most cases advisable to moisten the filter previously to passing the fluid through it; since this not only tends to accelerate the process, but also renders the solid particles less liable to be carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially such as are dissolved by acids, *e.g.*, sesquioxide of iron and lime. The common filtering paper of commerce seldom comes up to our wants in this respect, and I would therefore always recommend to wash it carefully with dilute hydrochloric acid whenever it is intended for use in *accurate analyses*. With the stronger sorts of paper this may be done by placing the paper cut in circular discs, in a layer of moderate thickness, in a shallow

porcelain dish, pouring over it a mixture of one part of hydrochloric acid or nitric acid with about nine parts of water, and letting it digest for several hours at a moderate heat. The fluid is then poured off, and the paper is repeatedly washed with water (finally with distilled water), until litmus paper is no longer reddened by the washings: the water is then drained off, and the entire layer is carefully transferred to a quire of blotting-paper, and left there until they can be taken off singly without injury; they are then hung up to dry on lines in a place free from dust. With the finer sorts of paper (Swedish paper) I prefer washing the filters in the funnel. To this end they are first sprinkled with a little moderately diluted hydrochloric or nitric acid, and then thoroughly washed with water, finally with distilled water. Filtering paper, to be considered good, must, besides being pure, also let fluids pass readily through, whilst yet completely retaining even the finest pulverulent precipitates, such as sulphate of baryta, oxalate of lime, &c. If a paper satisfying these requirements cannot be readily procured, it is advisable to keep two sorts, one of greater density for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles. The funnels must be of glass or porcelain (§ 16, 10); they are usually placed on an appropriate stand, to keep them in a fixed position. The stand shown in Fig. 1 is particularly well adapted for the reception of the small-sized funnels used in qualitative analyses.

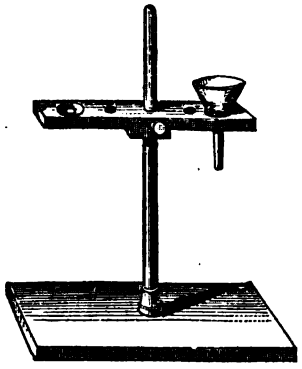


Fig. 1.

§ 6.

5. Decantation.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; as they will in such cases speedily subside to the bottom, thereby rendering it easy either to decant the supernatant fluid by simply inclining the vessel, or to draw it off by means of a syphon or pipette.

In cases where filtration or decantation are resorted to for the purpose of obtaining the solid substance, the latter has to be freed afterwards by repeated washing from the liquid still adhering to it.

The operation is called *washing* or *edulcoration*. The washing of precipitates collected on a filter is usually effected by means of a washing bottle, such as is shown in Fig. 2.

Fig. 2.

This consists of a flask or bottle, closed with a twice-perforated, snugly-fitting cork, through which pass two glass tubes, as in the figure. The outer end of the tube, *a*, is drawn to a moderately fine point. By blowing into the other tube, a stream of water is driven out from *a* with considerable force, which adapts the apparatus to removing precipitates from the sides of vessels as well as to washing them on filters. This form of washing-bottle serves for edulcoration with warm or even boiling water, provided the vessel itself has a uniformly thin bottom, so that it can be heated without fear of breaking. It is improved by binding about the neck a ring of cork, or winding it closely with smooth cord. It then may be handled with convenience when its contents are hot. [As it is usually inclined when in use, it is further improved by bending the lower part of the tube *a* (after it is fitted through the cork), so that its end closely approaches the bottom of the bottle at B. Its contents may then be used nearly to the last drop without need of so frequent replenishing.]

As the success of an analysis often depends upon the complete or proper washing of a precipitate, we may here remark that the operator must accustom himself to continue the process until he is certain that the object in view has been actually accomplished. In general, this is not the case until the precipitate has been perfectly freed from the liquid in which it was formed. The analyst must not be content to *guess* that a precipitate is thoroughly washed, but must *prove* that it is so, by applying appropriate tests. If the body to be removed is non-volatile, slow evaporation of a few drops of the last portions of the washings on a clean surface of glass or platinum, will usually serve to indicate the point at which the process may terminate.

There are four operations which serve to separate volatile substances from less volatile or from fixed bodies, viz., *evaporation*, *distillation*, *ignition*, and *sublimation*. The two former of these operations are applied exclusively to fluids, the two latter exclusively to solids.

§ 7.

6. Evaporation.

This operation is of very frequent occurrence. It serves to separate volatile fluids from less volatile or from fixed bodies (no matter whether solid or fluid), in cases where the residuary substance alone is of importance, whilst the evaporating matter is entirely disregarded;—thus, for instance, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to bring about crystallization of the salt; we resort to this process also for the purpose of removing the whole of the water of the menstruum from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form, &c. The evaporated water is entirely disregarded in either of these cases, the only object in view being to obtain, in the former case, a more concentrated fluid, and in the latter a dry substance. These objects are invariably attained by converting the fluid which is to be removed to the gaseous state. This is generally done by the application of heat; sometimes also by leaving the fluid for a certain time in contact with the atmosphere, or with an enclosed volume of air constantly kept dry by hygroscopic substances, such as concentrated sulphuric acid, chloride of calcium, &c.; or, lastly, in many cases, by placing the fluid in rarefied air, with simultaneous application of hygroscopic substances. As it is of the utmost importance in qualitative analyses to guard against the least contamination, and as an evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted, with proper expedition, over the flame of a spirit or gas-lamp, in a separate place free from dust and not exposed to draughts of air. If the operator has no place of the kind, he must have recourse to the much less suitable proceeding of covering the dish; the best way of doing this is to place over the dish a large glass funnel secured by a retort holder, in a manner to leave sufficient space between the rim of the funnel and the border of the dish; the funnel is placed slightly aslant that the drops running down its sides may be received in a beaker. Or the dish may also be covered with a sheet of filter paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid (see § 5); were common and unwashed filter paper used for the purpose, the sesquioxide of iron, lime, &c., contained in it, would dissolve in the vapors evolved (more especially if acid), and the solution dripping down into the evaporating fluid would speedily contaminate it. These precautions are necessary of course only in accurate analyses.

Fig. 8.

[In most ordinary cases, vessels may be covered with the very thin white paper used by grocers (tea-paper) without detriment, since the impurities that can find their way into solutions from so small a weight of paper, are too slight to affect common analyses.] Larger quantities of fluid are evaporated best in glass flasks standing aslant, covered with a cap of paper, over a charcoal fire or gas; or also in retorts. Evaporating processes at 212° are conducted in an appropriate steam apparatus, or in the water-baths shown in Fig. 3.

Evaporation to dryness, instead of being conducted over a free fire or lamp-flame, is best carried on either in a water or sand-bath or on a heated iron plate.

§ 8.

7. Distillation.

This operation serves to separate a volatile liquid from a less volatile or a fixed substance (no matter whether solid or fluid), where the object is to recover the evaporating fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporates, into the fluid state. A distilling apparatus consists consequently always of three parts, no matter whether admitting of separation or not. These three parts are—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2nd, an apparatus in which this vapor is cooled again or *condensed*, and thus reconverted to the fluid state; and 3rd, a vessel to receive the fluid thus reproduced by the condensation of the vapor (the distillate). For the distillation of

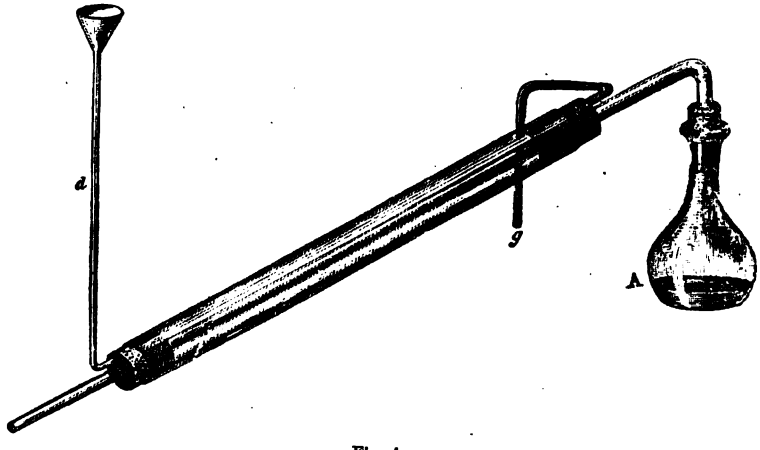


Fig. 4.

large quantities we use either a metallic apparatus (a copper still with head and condenser made of tin or pewter), or large glass

retorts; in analytical investigations we generally employ the apparatus shown in Fig. 4.

§ 9.

8. Ignition.

Ignition is, in a certain measure, for solid bodies what evaporation is with regard to fluids; since it serves (at least generally) to separate volatile substances from less volatile or from fixed bodies, in cases where the residuary substance alone is of importance. The process of ignition always presupposes the application of a high temperature, in which it differs from that of drying or exsiccation. The form or state which the eliminated substance assumes on cooling—whether it remains gaseous, as in the ignition of carbonate of lime; or assumes the liquid state, as in the ignition of hydrate of lime; or solidifies, as in the ignition of a mixture containing chloride of ammonium—is a matter of perfect indifference as regards the name given to the operation.

The process of ignition is mostly employed, as has just been said, to effect the elimination of a volatile body. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus the sesquioxide of chromium is converted by ignition into its insoluble modification, &c. In analytical investigations substances under examination are often ignited also, that the operator may from their deportment at a red heat draw a conclusion as to their nature in general; their fixity, their fusibility, the presence or absence of organic matter, &c.

Crucibles are the vessels made use of in ignition. In operations on a large scale Hessian or black-lead crucibles are used, heated by charcoal or coke; in analytical experiments small-sized crucibles or dishes are selected, of porcelain, platinum, silver or iron, or glass tubes sealed at one end, according to the nature of the substances to be ignited; these crucibles, dishes, or tubes are heated over a *Berzelius* spirit-lamp or a properly-constructed gas-lamp.

§ 10.

9. Sublimation.

The term *sublimation* designates the process which serves to expand solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration; the substance volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly to effect the separation of substances possessed of different degrees of volatility. Its application is of the highest importance in analysis for the detection

of certain substances, *e. g.* of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of volatility of the substances operated upon. In sublimations for analytical purposes we generally employ sealed glass tubes.

§ 11.

10. Fusion and Fluxing.

We designate by the term "fusion" the conversion of a solid substance into the fluid form by the application of heat; fusion is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term "fluxing" is applied to this process in cases where substances insoluble or difficult of solution in water and acids are by fusion in conjunction with some other body modified or decomposed in such a manner, that they or the new-formed compounds will subsequently dissolve in water or acids. Fusion and fluxing are conducted either in porcelain, silver, or platinum crucibles, according to the nature of the compound. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the ring of the spirit or gas-lamp. Triangles of thick iron wire, especially when laid upon the still stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures. Small quantities of matter are also often fused in glass tubes sealed at one end.

Resort to fluxing is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates. The flux most commonly used is carbonate of soda or carbonate of potassa, or, better still, a mixture of both in equal atomic proportions (see § 78). In certain cases, hydrate of baryta is used instead of the alkaline carbonates (see § 79). But in either case the operation is conducted in platinum crucibles.

I have to add here a few precautionary rules for the prevention of damage to the platinum vessels used in these operations. No substance evolving chlorine ought to be treated in platinum vessels; no nitrate of potassa, caustic potassa, metals, sulphides of the metals, or cyanides of the alkalies, should be fused in such vessels; nor ought readily deoxidizable metallic oxides, organic metallic salts, or phosphates to be ignited in them in the presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them directly to an intense charcoal fire, since the action of the ash, under such circumstances, gives readily rise to the formation of silicide of platinum, which renders the vessel brittle. It is always advisable to support the platinum crucible in which a process of ignition or fusion is to be conducted, on a triangle of platinum wire. [When platinum ves-

sels are ignited in the gas flame, especially over a blast lamp, they are liable to assume a dull and soiled aspect externally, and after prolonged use often become cracked with rifts, that at first are scarcely perceptible, but shortly extend so as to ruin the vessel. This detriment is prevented] and generally most kinds of stains may be removed from platinum apparatus by gently rubbing the surface with moist sea-sand as often as the lustre is impaired. The grains of sand must be polished and free from sharp angles. By the proper use of sand of good quality, the metal is not scoured, but *burnished*. If the stains or impurities in a platinum dish resist this treatment, bisulphate of potassa or borax should be heated in it to fusion for some time. The vessel is then cleaned with hot water, and finally, if needful, is burnished with sand as above described.

We have still to speak here of another operation which bears some affinity to fusion.

§ 12.

11. Deflagration.

We understand by the term "*deflagration*," in a more general sense, every process of decomposition attended with noise or detonation—(the *cause* of the decomposition is a matter of perfect indifference as regards the application of the term in this sense).

We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in a dry way, at the expense of the oxygen of another substance mixed with it (usually a nitrate or a chlorate), and connect with it the idea of a sudden and violent combustion attended with vivid incandescence and noise or detonation. Deflagration is resorted to either to produce the desired oxide—thus tersulphide of arsenic is deflagrated with nitrate of potassa to obtain arsenate of potassa;—or it is applied as a means to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid, by fusing them in conjunction with cyanide of potassium, and observing whether this process will cause deflagration or not, &c.

To attain the former object, the perfectly dry mixture of the substance under examination and of the deflagrating agent is projected in small portions into a red-hot crucible. Experiments of the latter description are invariably made with very minute quantities; the process is, in such cases, best conducted on a piece of thin platinum foil, or in a small spoon.

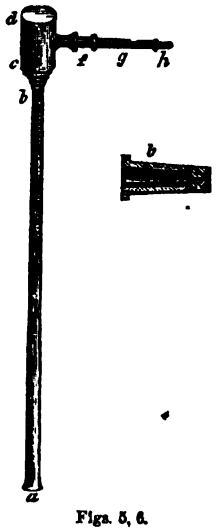
§ 13.

12. The Use of the Blowpipe.

This operation belongs exclusively to the province of analytical chemistry, and is of paramount importance in many analytical

processes. We have to examine here, 1, the apparatus; 2, the mode of its application; and, 3, the results of the operation.

The blowpipe (Fig. 5) is a small instrument, usually made of brass or German silver. It consists of three distinct parts; viz. 1st, a tube (*a b*), fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth; 2nd, a small cylindrical vessel (*c d*), into which *a b* is ground air-tight, and which serves as an air-chamber, and to retain the moisture of the air blown into the tube; and, 3rd, a smaller tube (*f g*), also fitted into the vessel (*c d*). This small tube, which forms a right angle with the larger one, is fitted at its aperture either simply with a finely perforated platinum plate, or more conveniently with a finely perforated platinum cap (*h*) ground on air-tight. The construction of the cap is shown in Fig. 6. It is, indeed, a little dearer than a simple plate, but it is also much more durable. Whenever the opening of the cap happens to be stopped up, the obstruction may be removed by heating the cap to redness before the blowpipe. [A cap of brass is in no way inferior to one of platinum. It may be cleaned by a needle, from the inside, and is much easier to obtain of the thickness requisite to withstand continued use.]



Figs. 5, 6.

The proper length of the blowpipe depends upon the distance to which the operator can see with distinctness; it is usually from eight to ten inches. The form of the mouthpieces varies. Some chemists like them of a shape to be encircled by the lips; others prefer the form of a trumpet mouthpiece, which is only pressed against the lips. The latter require less exertion on the part of the operator, and are accordingly generally chosen by those who have a great deal of blowpipe work.

The blowpipe serves to conduct a continuous fine current of air into a gas-flame, or into the flame of a candle or lamp. The flame of a candle (and equally so that of gas or of an oil lamp), burning under ordinary circumstances, is seen to consist of three distinct parts, as shown in Fig. 7, viz., 1st, a dark nucleus in the centre(*a*); 2nd, a luminous cone surrounding this nucleus (*e f g*); and, 3rd, a feebly luminous mantle encircling the whole flame (*b c d*). The dark nucleus is formed by the gases which the heat evolves from the wax or fat, and which cannot burn here for want of oxygen. In the luminous cone these gases come in contact with a certain amount of air insufficient for their complete

combustion. In this part, therefore, it is principally the hydrogen of the carbides of hydrogen evolved which burns, whilst the carbon separates in a state of intense ignition, which imparts to the flame the luminous appearance observed in this part. In the outer coat, the access of air is no longer limited, and all the gases not yet burned are consumed here. This part of the flame is the hottest; oxidizable bodies oxidize therefore with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, viz. high temperature, and an unlimited supply of oxygen. This outer part of the flame is therefore called the *oxidizing flame.*

Fig. 7.

On the other hand, oxides having a tendency to yield up their oxygen, suffer *reduction* when placed within the *luminous* part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed carbide of hydrogen present in this sphere. The luminous part of the flame is therefore called the *reducing flame.*

Now the effect of blowing a fine current of air across a flame, is first to alter the shape of the latter, which, from tending upward, is now driven sideways in the direction of the blast, and at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase of the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the current, will always depend upon the precise object in view, viz., whether the operator wants a *reducing* or an *oxidizing* flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a tube, terminating in a flat top with a somewhat slantingly downward-turned slit 1 centimètre long and 1½ to 2 millimètres wide; as with the use of gas the operator is enabled to control and regulate not only the blowpipe flame, but the gas stream also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some moveable metallic support, such as, for instance, the ring of *Bunsen's* gas lamp for supporting dishes, &c.

Fig. 8 shows the flame for reducing, Fig. 9 the flame for oxidizing. The luminous parts are shaded.

The *reducing* flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner

bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat

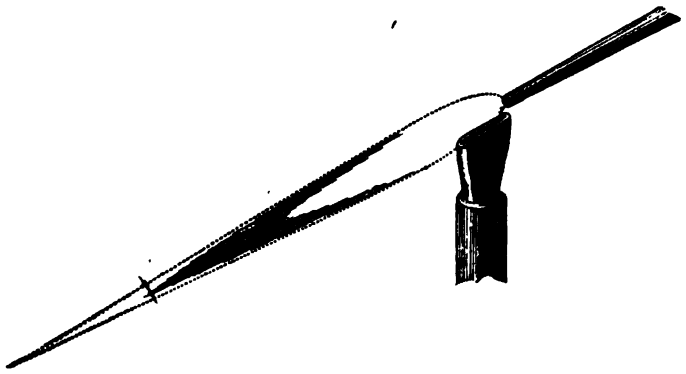


Fig. 8.

beyond the apex of the inner cone. To produce the *oxidizing* flame, the gas is lowered, the jet of the blowpipe pushed a little further into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas, and an inner pointed, bluish cone, slightly luminous towards the apex, is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect their fusion; but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion. An oil-lamp with broad wick of proper thickness may be used instead of coal-gas; a thick wax candle also will do. For an oxidizing flame, a small spirit-lamp will in most cases answer the purpose.

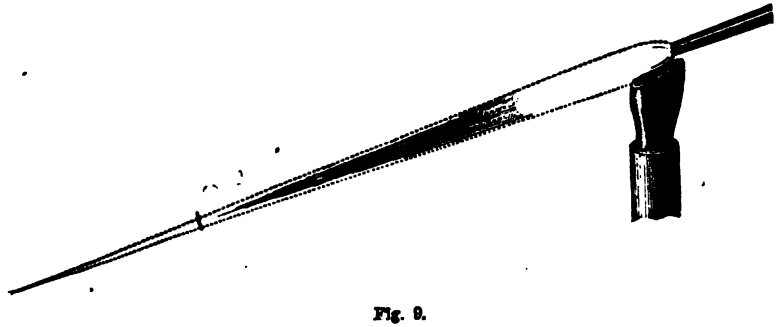


Fig. 9.

The *current* is produced with the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by

practising for some time to breathe calmly with puffed-up cheeks, and with the blowpipe between the lips; with a little patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood-charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, &c., or in trying the fusibility of bodies. The substances to be operated upon are put into small conical cavities scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame, evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame, the metallic fumes are re-oxidized, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colors leading to the detection of the metals. Thoroughly-burnt pieces of charcoal only should be selected for supports in blowpipe experiments, as imperfectly-burnt pieces are apt to spirt and throw off the matter placed on them. The charcoal of the wood of pine, linden, or willow is greatly preferable for supports to that of harder and denser woods. Smooth pieces ought to be selected for supports, as knotty pieces are apt to spirt when heated, and throw off the matter placed on them. The most convenient way is to saw the charcoal of well-seasoned and straight-split pinewood into parallelopipedic pieces, and to blow or brush off the dust; they may then be handled without fear of soiling the hands. Those sides alone are used on which the annual rings are visible as circles or segments, as on the other sides the fused matters are apt to spread over the surface of the charcoal (*Berzelius*).

The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—1st, its infusibility; 2nd, its low conducting power for heat, which admits of substances being heated more strongly upon a charcoal than upon any other support; 3rd, its porosity, which makes it imbibe readily fusible substances, such as borax, carbonate of soda, &c., whilst infusible bodies remain on the surface; 4th, its power of reducing oxides, which greatly contributes to effecting the reduction of oxides in the inner blowpipe flame.

We use *platinum wire*, and occasionally also *platinum foil*, in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them, and to watch the phenomena attending the solution, and mark the color of the bead.

The wire, which should be about the thickness of lute-strings, is

cut into lengths of three inches, and each length bent at both ends into a small loop (Fig. 10.)

Fig. 10.

When required for use, the loop is moistened with a droplet of water, then dipped into the flux, and the portion adhering exposed to the flame of a gas or spirit-lamp. The bead produced, which continues to adhere to the loop, is let cool, then moistened again, a small portion of the substance to be examined added to it, and the loop finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

What renders the application of the blowpipe particularly useful in chemical experiments is the great expedition with which the intended results are attained. These results are of a twofold kind, viz., either they afford us simply an insight into the general properties of the examined body, and enable us accordingly only to determine the *class* to which it belongs, *i. e.*, whether it is fixed, volatile, fusible, &c.; or the phenomena which we observe enable us at once to recognise the particular body which we have before us. We shall have occasion to describe these phenomena when treating of the deportment of the different substances with reagents.

For most analytical purposes, the blowpipe may be replaced with great advantage and convenience by the non-luminous and smokeless flame of the Bunsen gas-lamp, which is described in the subsequent paragraphs.

§ 14.

13. Alcohol and Gas-lamps.

In chemical analysis the operator has constant occasion to submit substances to the influence of heat in evaporations, ignitions, &c. As for the most part small quantities of matter are employed, the requisite heat may be usually obtained from suitable lamps, for which *alcohol*, or better when it is at hand, *illuminating gas*, may serve as fuel.

Alcohol or Spirit-Lamps are of two kinds; the common or plain *spirit-lamp* (Fig. 13) is made of glass, has a ground glass cap and a brass wick-holder, and suffices to give a moderate heat for small operations. *The Berzelius lamp* has a hollow wick with double draught, and is much more powerful in its effects.

The form shown in Fig. 11 is convenient and serviceable. It is adjustable to any desired position upon a brass stand, which also bears a stout brass ring for supporting heavy vessels, and a second ring of slender iron wire to carry a triangle for sustaining crucibles

in the processes of ignition and fusion. The part enclosing the wick and the vessel containing the spirit of wine must be in separate pieces, connected together by means of a narrow tube; otherwise disagreeable explosions are apt to occur on lighting the lamp. The chimney must not be too narrow. The stopper on the mouth, through which the spirit of wine is poured in, must not fit air-tight.

[The Rosè and MITSCHERLICH lamps are of essentially the same construction. The stand of the former usually has a flat base, covered with a plate of porcelain, which is convenient for resting hot vessels upon. The latter is provided with a glass feeding reservoir arranged so as to maintain the alcohol about the wick, at a constant level.] Fig. 12 exhibits a triangle of platinum wire secured within a larger one of iron wire. It is useful for supporting crucibles while heating to redness.

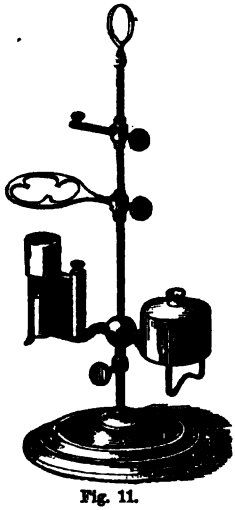


Fig. 11.

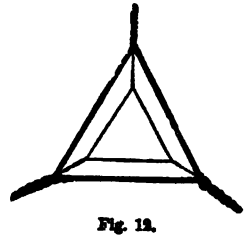


Fig. 12.

Fig. 13.

Glass vessels, more particularly beakers, which it is intended to heat over the lamp, are most conveniently rested on a circular piece of gauze made of fine iron wire such as is used in the making of sieves of medium fineness.

Of the many gas-lamps proposed, *Bunsen's*, as shown in its simplest form in Fig. 15, is the most convenient; *a b* is a foot of cast-iron measuring 7 centimètres in diameter. In the centre of this is fixed a square brass box, *c d*, which slightly slants towards the top; the sides of this box are 25 millimètres high and 16 millimètres wide; it has a cylindric cavity 12 millimètres deep and 10 millimètres in diameter. Each side of the box has 4 millimètres from the upper rim, a circular aperture of 8 millimètres diameter,

leading to the inner cavity. One of the sides has fitted into it, about 1 millimètre below the circular aperture, a tube, *d*, to which is attached a vulcanized india-rubber hose, which serves to convey

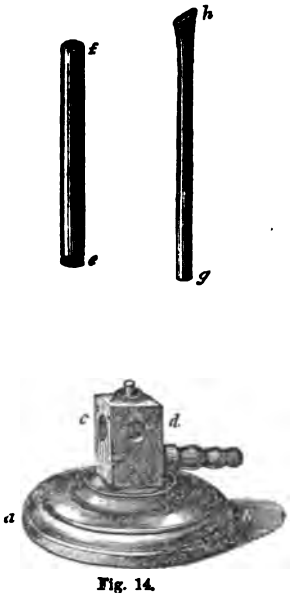


Fig. 14.

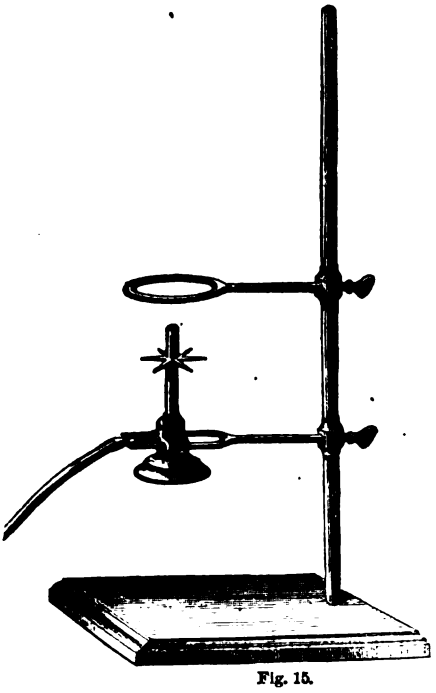


Fig. 15.

the gas to the apparatus. This tube is turned as shown in Fig. 14; it has a bore of 4 millimètres diameter. The gas conveyed into it through the india-rubber re-issues from a tube placed in the centre of the cavity of the box. This tube, which is 4 millimètres thick at the top, thicker at the lower end, projects 3 millimètres above the rim of the box; the gas issues from a narrow opening which appears formed of 3 radii of a circle, inclined to each other at an angle of 120°. The length of each radius is 1 millimètre, the opening $\frac{1}{3}$ millimètre wide; *e f* is a brass tube 75 millimètres long, open at both ends, and having an inner diameter of 9 millimètres; the screw at the lower end of this tube fits into a nut in the upper part of the cavity of the box. With this tube screwed in, the lamp is completed. On opening the stop-cock, the gas rushes from the opening into tube *e f*, when it mixes with the air coming in through the circular apertures (*c*). When this mixture is kindled at *f*, it burns with a straight, bluish flame, entirely free from soot, which may be regulated at will by opening the stop-cock more or less; a partial opening of the cock suffices to give a

flame fully answering the purpose of the common simple spirit lamp; whilst, with the full stream of gas turned on, the flame, which will now rise up to 2 decimètres in height, burning with a roaring noise, affords a most excellent substitute for the Berzelius lamp. When the gas burns low, it sometimes happens that the flame recedes to the bottom of the tube *f e*, and burns there unmixed with air and with smoke. This difficulty is remedied by bending a bit of wire-gauze over the top of the tube *f e*, so as to form a movable cap. Flasks, &c., which it is intended to heat over the gas-lamp, are most conveniently supported on wire-gauze. If it is wished to use the gas-lamp for blowpipe operations, the tube *g h* must be inserted into *e f*; this tube terminates in a flattened top slanting at an angle of 68° to the axis, and having an opening in it 1 centimètre long and 1½ to 2 millimètres wide; its insertion into *e f* serves to close up the air-apertures in the box, and pure gas, burning with a luminous flame, issues accordingly now from the top of the tube. Fig. 15 shows the apparatus complete, fixed in the forked iron stand; this arrangement permits the lamp being moved backward and forward between the prongs of the fork, and up and down the pillar of the stand. The movable ring on the same pillar serves to support the object to be operated upon. The 6 radii round the tube of the lamp serve to support a sheet-iron chimney (see Fig. 17), or a porcelain plate used in quantitative analyses.

When it is necessary to heat a crucible to an intense red, or even to a white heat, a blast-lamp must be employed. The effect of the Bunsen burner may, however, be greatly increased by a suitable clay chimney, such as recommended by *O. L. Erdmann*. Fig. 16 represents the arrangement. The chimney has a height of 4½ inches, and is 3 inches wide in the clear. The walls are three-eighths of an inch thick. In order to make the gas-lamp serve as a substitute for the blowpipe in experiments of reduction, oxidation, fusion, &c., or in observing the coloration imparted by various substances to the flame, *Bunsen** has arranged it as shown in Fig. 17. Here is seen a ring, *a*, which, being movable up and down on a screw, serves to regulate with perfect nicety the access of air to the flame. Again a conical sheet-iron chimney, *b*, which has a diameter above of 30 millimètres, below of 55 millimètres, is so placed on the radii *c c*, that the tube *d* is in its axis and terminates 45 millimètres below its upper edge. This chimney

Fig. 16.

* Ann. d. Chem. v. Pharm. 111, 257.

has the effect of producing an elongated flame of a shape like that represented in the Figure, which burns quietly and with uniformity. By careful examination, this flame is perceived to be made up of an interior part and two surrounding envelopes. The former corresponds to the dark centre of the ordinary luminous flame, and contains the unconsumed mixture of gas and air. If the gas-cock be so turned that the point of this interior portion is on a level with the top of the chimney, the flame becomes perfectly steady and definite in its parts. By this means it may always be re-produced with the same form and qualities when desired. The mantle which immediately surrounds the interior part contains unconsumed hydro-carbons; the exterior blue envelope consists of the final products of combustion. According to Bunsen's calcu-

Fig. 17.

Fig. 18.

lation, the hottest point in the flame has a temperature of about 2300° C. (4172° Fah.) It is situated in the mantle that lies within the outer blue envelope, and in a horizontal zone which occupies a few millimètres of space above and below the point of the inner mantle. This *zone of fusion*, as it may be called,

serves to examine the deportment of bodies at a temperature of about 2300° C. Its external border acts as an *oxidizing flame;* within it has the effect of a *reducing flame*, and most powerfully just above the point of the interior part of the flame. The Bunsen lamp, thus regulated, serves admirably for observing the coloring which many substances communicate to flame, and which furnishes the most ready and sensitive test of the presence of some bodies, enabling the operator to discover the slightest traces of them when all other means of recognition are useless. In the next paragraph this subject comes under notice. Here we must further state that a great advantage of the gas over the blow-pipe-flame consists in the fact that, by means of a suitable holder, the substance under examination may be kept for any length of time in a given part of the flame. Such a holder is represented in Fig. 18. The arm *a* is maintained at any desired height on the rod *c*, by means of the spring slide *b; d* is a glass tube which passes over the arm *a*. Into one end of it a platinum wire of about 0.145 millimètre diameter is fused, which is bent to a loop at its free extremity. By bringing the moistened platinum loop in contact with the powder of the substance that is to be examined, a portion of it adheres; and when the loop is held for a time near the flame and finally within it, the substance sinters or fuses firmly upon the wire. Matters that decrepitate must first be ignited in a covered platinum vessel. For testing liquids the wire of the loop is flattened by a few blows with a hammer; then, if dipped into the substance, it lifts a drop, which, by holding near the flame, slowly evaporates, and the residue, if any, may be brought into the zone of fusion (*Bunsen*).

§ 15.

14. Colored Flames and Spectral Analysis.

Many substances, when brought into a colorless or non-luminous flame, color it in a remarkable manner. The colorations are, in many cases, characteristic of the elements yielding them, and furnish excellent means of detecting the latter, even in the minutest quantities, with great ease and certainty. Thus soda-salts tinge the flame yellow; potassa-compounds violet; lithia-salts carmine-red; and on account of this peculiarity they may be distinguished from each other by the simplest experiments.

The Bunsen lamp, with chimney, previously described (Fig. 17), is especially adapted to such observations. The substance to be tested is brought by means of the platinum wire-loop, Fig. 18, into the zone of fusion of the gas-flame. The alkalies and alkaline earths are most remarkable in their coloring effects on the flame. If we compare together various salts of the same base, we find that they

all, if volatile at the temperature of the flame, give the same color, but the color differs in intensity, being strongest with the most volatile salts, and *vice versâ*. Thus, chloride of potassium gives a deeper tinge to the flame than carbonate of potassa, and carbonate a stronger than silicate of potassa. Sometimes a non-volatile compound is made to exhibit a characteristic tint by the addition of some flux or decomposing agent. Silicates which contain but a few *per cent.* of potassa, and of themselves do not color the flame, give a coloration after heating with some pure sulphate of lime, which decomposes them, producing silicate of lime and volatile sulphate of potassa.

In mixtures of several substances which may be individually detected without difficulty, when they exist separately, it usually happens that a mixed and indecisive coloration is produced, or one substance masks all the others. Thus, in a mixture of soda and potassa-salts, only a soda-flame—in one of baryta and strontia-salts, only a baryta-flame is evident to the unassisted eye. We have recently learned two methods of dissecting these mixed flames so as to recognize their component colors with surprising facility and distinctness.

The first method, introduced into chemistry by *Cartmell*,* and further developed by *Bunsen*† and *Merz*,‡ consists in observing the colored flames through colored media (stained-glass, indigo-solution, &c.). These act by extinguishing the color of one metal and thus developing that of the other. A mixture of soda and potassa, which to the eye has a pure yellow flame, when seen through a deep-blue cobalt glass or a solution of indigo, exhibits the violet tint of potassa without any traces of the yellow soda-flame. The apparatus for these observations is simple, viz:

1. A hollow prism, made of plate glass, Fig. 19, whose principal section forms a triangle, with two sides of 150 millimètres and one of 35 millimètres long. The solution with which it is filled is prepared by dissolving 1 part of indigo in 8 parts of fuming oil-of-

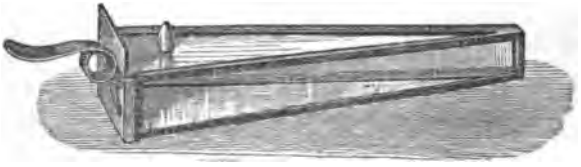


Fig. 19.

vitriol, adding 1500 to 2000 parts of water and filtering. In use, the prism is held close before the eye and moved horizontally, so

* Philosophical Magazine, XVI. 328.
† Ann. d. Chem. u. Pharm. III. 257.
‡ Jour. f. Prakt Chem. 80, 487.

as to cause the light of the colored flame to pass into the eye through successively thicker portions of the absorbing medium.

2. A blue, a violet, a red and a green glass. The blue is colored by protoxide of cobalt; the violet, by sesquioxide of manganese; the red, by suboxide of copper; and the green, by sesquioxide of iron and oxide of copper. The stained glasses found in commerce and employed for ornamenting windows, generally possess the requisite shades of color. The appearance of the colored flames produced by various bodies, when seen through these media, and the combinations which serve to recognize individual substances, are described in Section III.

The second method—that of *spectral analysis*, discovered by *Kirchhoff* and *Bunsen*, consists in letting the rays of the colored flame, after passing through a narrow slit, traverse a prism, and in observing the spectrum thus produced by means of a telescope. Each of the metals which give color to the flame, thus yields a peculiar spectrum, formed in some cases, as in that of baryta, of many contiguous colored lines; in others of two more distant lines of different color, as shown by lithia; or, again, of a single line, as in case of soda and thallium. These spectra are characteristic in two respects, viz. 1, in the definite color of the spectral lines; and 2, in the invariable relative position they occupy.

The last named fact enables us to detect, without difficulty in most cases, all the spectrum-giving ingredients of a mixture. Thus, when potassa, soda and lithia-salts are brought together into the *spectroscope*, the lines characteristic of each metal appear in the utmost purity at one view. [Very minute traces of some elements do not, however, exhibit their spectra in presence of large quantities of other substances.]

Kirchhoff and *Bunsen* have described two instruments adapted to spectral observations. The larger and more complete is figured in *Poggendorff's Ann.* 113, 374; also *Fresenius' Zeitschrift für analytische Chemie*, 1862. 49. The smaller, simpler, and cheaper instrument, which is perfectly adapted for ordinary uses, is here described. It is represented in Fig. 20.

The triangular glass prism, whose refracting surfaces are circles of about 25 millimètres in diameter, is placed at the centre of a circular iron plate, *A*, to which it is secured by a clamp. To the same iron plate the three brass tubes *B*, *C*, *D*, are permanently attached. Each tube is soldered to a block of metal (shown enlarged in Fig. 21), which is secured by means of two screws to the iron plate, after the tube has been brought into its proper position. *B* is the telescope through which the spectrum is seen. It has an objective of 20 millimètres aperture, and magnifies about six diameters.

The tube *C* has at its outer extremity the vertical slit through

which the rays of the flame pass on their way to the prism. The tube *D*, at its outer end, bears a narrow, horizontal scale photographed on glass. In use, this scale is illuminated by the flame of a lamp placed immediately before it.

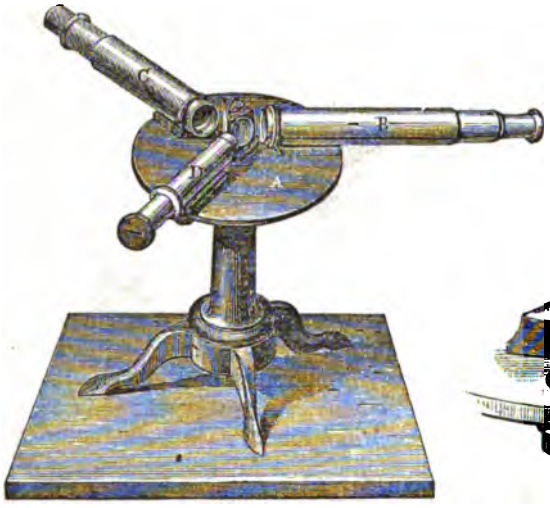


Fig. 20.

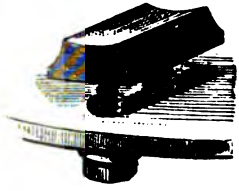


Fig. 21.

The axes of the tubes *B* and *D* are equally inclined to one face of the prism. The tube *C* is opposite to the other face. By this arrangement, the spectrum produced by refraction of the light that traverses *C*, and the image of the scale in *D*, produced by total reflection, are seen together by the eye looking into *B*, and thus the position of the colored lines may be read off in degrees of the scale. The prism is placed nearly in a position in which the deviation of the rays of the soda line is a minimum, and the telescope is so situated that the centre of the field lies equidistant between the red and the violet potassa lines.

Four inches from the slit in *C* is placed the colorless flame of Bunsen's lamp, Fig. 17. It is so regulated that the upper edge of the chimney lies about $\frac{1}{16}$ of an inch below the bottom of the slit. A bead of sulphate of potassa is now brought into the flame (as described on page 25,) and the instrument is so adjusted that the spectrum becomes as bright as possible. To cut off external light, a black cloth, having three slits corresponding to the three tubes, is hung over them and the prism.

[A cheap and excellent spectroscope, planned by Prof. J. P. Cooke, of Harvard College, and made by Alvan Clark, of Cambridgeport, Mass., has the prism inclosed in a circular wooden box into which the three tubes are firmly fixed.]

[The spectra which are the most serviceable for analytical pur-

poses are mapped on plate I. The scale employed is that of Kirchhoff and Bunsen's instrument, in which the degree 50 coincides with the yellow sodium line. The topmost scale gives the positions of some of the more important dark lines (Fraunhofer's), of the solar spectrum, which are distinguished by the letters *A*, *B*, *C*, &c., and *a* and *b*. The limits of the seven colors are indicated with sufficient accuracy by the vertical lines drawn below each spectrum. The long dashes of black drawn at the upper edge of the spectra of potassa, rubidia, cæsia and soda, represent broad, continuous bands of color. The proper *spectral lines* are shown at the lower edge of each scale. The width of each line is seen from the number of degrees it covers. Its brightness is indicated by its vertical depth in the engraving. The most characteristic or important lines are designated by the Greek numerals. Special notice of them is given in Section III.

In using the spectroscope it is not always sufficient to perceive a line with its appropriate color; its position with relation to known standards must be likewise ascertained. This is done by making for each spectroscope a diagram of the spectra, similar to plate I. For most purposes, it is however only needful to map the more important lines. Any arbitrary scale being drawn, the lines are placed against degrees corresponding to those seen in the spectroscope, when beads of the purest accessible compounds of the various alkalies and alkaline earths are placed in the flame. To insure uniformity the left edge of the soda line, which is rarely absent even in specially prepared salts, is brought to coincide with the degree 50° or 100° of the scale of the instrument. To the position once adopted, the scale must always be brought before taking observations, if by any means it has been disturbed.]

In many respects the spectroscope opens a new era in chemical analysis, for with its aid we are able to detect quantities of substances that are not recognizable in any other manner. At the same time the results possess the utmost possible certainty, and are arrived at in a few moments.

APPENDIX TO SECTION I.

§ 16.

Apparatus and Utensils.

As many students of chemical analysis might find some difficulty in the selection of the proper apparatus, &c., I append here a list of the articles which are required for the performance of simple

experiments and investigations, together with instructions to guide the student in the purchase or making of them.

1. A Spirit-Lamp with Double Draught (§ 14, Fig. 11).

2. A Plain Spirit-Lamp of Glass (§ 14, Fig. 13), or instead of the above, when gas is at hand, a Bunsen's Gas-lamp with chimney (§ 14, Figs. 14, 15 and 17).

3. A Blowpipe (see § 13).

4. A Platinum crucible which will contain about a quarter of an ounce of water, with a cover of the form of a shallow dish; it must not be too deep in proportion to its breadth.

5. Platinum foil, as smooth and clean as possible, and not very thin: length about 1½ inches; width about 1 inch.

6. Platinum wire (see § 13, and § 14, Figs. 10 and 18); three or four stronger and as many finer wires are amply sufficient. They are kept most conveniently in a glass half filled with dilute hydrochloric acid, most of the beads being dissolved by that fluid when left in contact with it for some time; the wires may thus be always kept clean.

7. A Stand with twelve test tubes (Fig. 17); 6 to 8 inches is about the proper length of the tubes; from ½ to one inch the proper

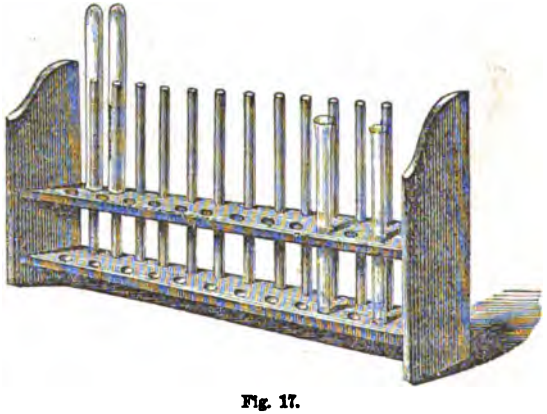


Fig. 17.

width. The pegs on the upper shelf serve for the clean tubes, which may thus be always kept dry and ready for use. The tubes must be made of thin white glass, and so well annealed that they do not crack, even though boiling water be poured into them. The rim must be quite round, and slightly turned over; it ought not to have a lip, as this is useless, simply preventing the tube being closely stopped with the finger, and also hindering the agitation of its contents.

8. Several beaker glasses and small retorts of thin, well annealed glasses.

9. SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN CRUCIBLES. Those of the royal manufacture of Berlin are unexceptionable, both in shape and durability.

10. SEVERAL GLASS FUNNELS of various sizes. Their sides must incline at an angle of 60°, and merge abruptly into the neck.

11. A WASHING BOTTLE of a capacity of about a pint (see § 6).

12. SEVERAL GLASS RODS AND GLASS TUBES. The latter are bent, drawn out, &c., over a Berzelius spirit-lamp, or over the gas-lamp; the former are rounded at the ends by fusion.

13. A selection of small WATCH GLASSES.

14. A small AGATE MORTAR.

15. A pair of small STEEL or BRASS PINCERS, about four or five inches long.

16. A WOODEN FILTERING STAND (see § 5).

17. A TRIPOD of thin iron, to support the dishes, &c., which it is intended to heat over the small spirit or gas-lamp.

18. The COLORED GLASSES mentioned in § 15, especially blue and green.

SECTION II.

REAGENTS.

§ 17.

A VARIETY of phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases liquids change their color, in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, &c. Now, if these phenomena are very striking, and attendant only upon the action of two definite bodies upon one another, it is obvious that the presence of one of these bodies may be detected by means of the other: if we know, for instance, that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that if, upon adding bartya to any liquid, we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called *reagents*.

According to the different objects attained by their application we make a distinction between *general* and *special* reagents. By *general* reagents we understand those which serve to determine the *class* or *group* to which a substance belongs; and by *special* reagents those which serve to detect and determine bodies individually. That the line between the two divisions cannot be drawn

with any degree of precision, and that one and the same substance is often made to serve both as a general and special reagent, cannot well be held a valid objection to this classification, which, in fact, is simply intended to induce a habit of employing reagents always for a settled purpose—viz., either simply to find out the *group* to which the substance under examination belongs, or to determine the latter *individually*.

Now whilst the usefulness of *general* reagents depends principally upon their efficiency in strictly characterizing groups of bodies, and often effecting a complete separation of the bodies belonging to one group from those belonging to another, that of *special* reagents depends upon their being *characteristic*, and upon their being *sensitive*. We call a reagent *characteristic*, if the alteration produced by it, in the event of the body tested for being present, is so distinctly marked as to admit of no mistake. Thus, iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena produced by these reagents—viz., the separation of metallic copper and of globules of mercury, admit of no mistake. We call a reagent *sensitive* or *delicate*, if its action is distinctly perceptible, even though a very minute quantity only of the substance tested for be present; such is, for instance, the action of starch upon iodine.

Very many reagents are *both* characteristic and delicate; thus, for instance, terchloride of gold for protoxide of tin; ferrocyanide of potassium for sesquioxide of iron and oxide of copper, &c.

I need hardly mention that, as a general rule, reagents must be chemically pure—*i. e.*, they must consist purely and simply of their essential constituents, and must contain no admixture of foreign substances. We must therefore make it an invariable rule to *test the purity of our reagents before we use them*, no matter whether they be articles of our own production or purchased. Although the *necessity* of this is fully admitted on all hands, yet we find that in *practice* it is too often neglected: thus it is by no means uncommon to see alumina entered among the substances detected in an analysis, simply because the solution of potassa used as one of the reagents happened to contain that earth; or iron, because the chloride of ammonium used was not free from that metal. The directions given in this section for testing the purity of the several reagents, refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "*addition in excess*," "*supersaturation*," &c., often induce novices to suppose that they cannot add *too* much of the reagent, and thus some will *fill* a test

tube with acid, simply to *supersaturate* a few drops of an alkaline fluid, whereas *every drop* of acid added, after the neutralization point has once been reached, is to be looked upon as an *excess* of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent, when added in insufficient quantity, often produces phenomena quite different from those which will appear if the same reagent be added in excess: *e. g.*, a solution of chloride of mercury yields a *white* precipitate, if tested with a *small* quantity of hydrosulphuric acid; but if treated with the same reagent *in excess*, the precipitate is *black*. Experience has, however, proved that the most common mistake beginners make, is to add the reagents too copiously. The reason why this over-addition must impair the accuracy of the results, is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that therefore they may be the more readily overlooked the nearer we approach these limits by diluting the fluid.

No special and definite rules can be given for avoiding this source of error; a general rule may, however, be laid down, which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: *let the student always reflect, before the addition of a reagent, for what purpose he applies it, and what are the phenomena he intends to produce.*

We divide reagents into two classes, according to whether the state of fluidity which is indispensable for the manifestation of the action of reagents upon the various bodies, is brought about by the application of heat, or by means of liquid solvents; we have consequently, 1. *Reagents in the humid way;* and 2, *Reagents in the dry way.* For greater clearness we subdivide these two principal classes as follows:—

A. REAGENTS IN THE HUMID WAY.

I. Simple Solvents.

II. Acids (and Halogens).

a. Oxygen acids.

b. Hydrogen acids and halogens.

c. Sulphur acids.

III. Bases (and Metals).

a. Oxygen bases.

b. Sulphur bases.

IV. Salts.

a. Of the alkalies.

b. Of the alkaline earths.

c. Of the oxides of the heavy metals.

V. Coloring Matters and Indifferent Vegetable Substances.

B. REAGENTS IN THE DRY WAY.

I. Fluxes.

II. Blowpipe reagents.

A. REAGENTS IN THE HUMID WAY.

I. Simple Solvents.

Simple solvents are fluids which do not enter into chemical combination with the bodies dissolved in them; they will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is in a measure dependent upon the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, color, &c.) are not destroyed by the solvent. (See § 2.)

§ 18.

1. Water (H O).

Preparation.—Pure water is obtained by distilling spring water from a copper still, with head and condenser made of pure tin, or from a glass retort; which latter apparatus, however, is less suitable for the purpose. The distillation is carried to about three-fourths of the quantity operated upon. If it is desired to have the distilled water perfectly free from carbonic acid, and carbonate of ammonia, the portions passing over first must be thrown away. In the larger chemical, and in most pharmaceutical laboratories, the distilled water required is obtained from the steam apparatus which serves for drying, heating, boiling, &c. Rain water collected in the open air may in many cases be substituted for distilled water.

Tests. –Pure distilled water must be colorless, inodorous, and tasteless, and must leave no residue upon evaporation in a platinum vessel. Sulphide of ammonium must not alter it (copper, lead, iron); its transparency must not be in the least impaired by basic acetate of lead (carbonic acid, carbonate of ammonia), nor, even after long standing, by oxalate of ammonia (lime), chloride of barium (sulphates), or nitrate of silver (metallic chlorides).

Uses.—We use water* principally as a simple solvent for a great variety of substances; the most convenient way of using it is with the washing bottle (see § 6, Fig. 2), by which means a large or fine stream may be obtained. It serves also to effect the conversion of several neutral metallic salts (more particularly terchlo-

* In analytical experiments we use only *distilled* water; whenever, therefore, the term "water" occurs in the present work, distilled water is meant.

ride of antimony and the salts of bismuth) into soluble acid, and insoluble basic compounds.

§ 19.

2. Alcohol ($C_4 H_6 O_2$).

Preparation.—Two sorts of alcohol are used in chemical analysis: viz., 1st, spirit of wine of 0·83 or 0·84 *spec. gr.* (= 91 to 88 per cent. by volume, *spiritus vini rectificatissimus* of the shops); and 2nd, absolute alcohol. The latter may be prepared sufficiently absolute for most purposes, by bringing together in a retort or still 1 part of fused chloride of calcium, and 2 parts of commercial alcohol of about 90 *per cent.*, digesting two or three days until the chloride of calcium is dissolved and then slowly distilling. The distillate is tested as to its *sp. gr.* from time to time, and the first portions which are lighter than 0.81 (= 96.5 per cent. by volume,) are reserved as absolute alcohol; those passing over later are separately collected.

Tests.—Pure alcohol must completely volatilize, and ought not to leave the least smell of fusel oil, when rubbed between the hands; nor should it redden litmus paper. When kindled, it must burn with a faint bluish, barely perceptible flame.

Uses.—Alcohol serves (*a*), to effect the separation of bodies soluble in this fluid from others which do not dissolve in it, *e.g.*, of chloride of strontium from chloride of barium; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, *e.g.*, gypsum, malate of lime; (*c*) to produce various kinds of ether, *e.g.*, acetic ether, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, mostly with the co-operation of an acid, certain peroxides and metallic acids, *e.g.*, binoxide of lead, chromic acid, &c.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boracic acid, strontia, potassa, soda, and lithia.

§ 20.

3. Ether ($C_4 H_5 O$).

4. Chloroform ($C_2 H Cl_3$).

5. Sulphide of Carbon ($C S_2$).

These solvents find but very limited application in the analysis of inorganic bodies. They are chiefly used to detect and isolate iodine and bromine. Chloroform and sulphide of carbon are much preferable to ether for this purpose.

These substances are most conveniently purchased, as their preparation on the small scale is troublesome.

Tests.—*Ether* must have a sp. gr. of 0.725, and must require 9 parts of water for its solution. The solution must not affect test

papers. Placed upon a watch glass, it must evaporate at ordinary temperatures rapidly and completely.

Chloroform must be colorless and have a sp. gr. of 1.49. It must be free from acid reaction, and not be rendered turbid by solution of nitrate of silver. When agitated in a tube with two volumes of water, it must not suffer perceptible diminution of bulk. It must evaporate easily and completely at common temperatures.

Sulphide of Carbon must be colorless, without action on carbonate of lead, and must volatilize readily and perfectly at usual temperatures.

II. ACIDS AND HALOGENS.

§ 21.

The acids—at least those of more strongly pronounced character—are soluble in water. The solutions taste acid, and redden litmus paper. Acids are divided into oxygen acids, sulphur acids, and hydrogen acids.

The *oxygen acids*, produced generally by the combination of a non-metallic element with oxygen, combine with water in definite proportions to hydrated acids. It is with these hydrates that we have usually to do in analytical processes; they are commonly designated by the name of "free acids," as the accession of the water does not destroy their acid properties. In the action of hydrated acids upon oxides of metals, the oxide takes the place of the water of hydration, and an *oxygen salt* is formed ($H O, S O_3 + K O = K O, S O_3 + H O$). Where these salts are the product of the combination of an acid with a strong base, their reaction (supposing the combining acid also to be a strong acid) is neutral; the salts formed with weaker bases, for instance, with the oxide of a heavy metal, generally show acid reaction, but are nevertheless called neutral salts, if the oxygen of the base bear the same proportion to that of the acid in which it is found in the distinctly neutral salts of the same acid, or, in other terms, if it corresponds with the saturation capacity of the acid. Sulphate of potassa ($K O, S O_3$) has a neutral reaction, whilst the reaction of sulphate of copper ($Cu O, S O_3$) is acid; yet the latter is nevertheless called neutral sulphate of copper, because the oxygen of the oxide of copper in it bears a proportion of 1 : 3 to that of the sulphuric acid, which is the same proportion as the oxygen of the potassa bears to that of the sulphuric acid in the confessedly neutral sulphate of potassa.

The *hydrogen acids* are formed by the combination of the salt radicals with hydrogen. Most of these possess the characteristic properties of acids in a high degree. They neutralize oxygen bases with formation of *haloid salts* and water, $H Cl$ and $Na O =$

Na Cl and H O, — 3 H Cl and $Fe_2 O_3 = Fe_2 Cl_3$ and 3 H O. The haloid salts produced by the action of powerful hydrogen acids upon strong bases, have a neutral reaction; whilst the solutions of those haloid salts which have been produced by the action of powerful hydrogen acids upon weak bases (such as the oxides of the heavy metals), show acid reactions.

The *sulphur acids* are more frequently the result of the combination of metallic than of non-metallic elements with sulphur; they combine with sulphur bases to *sulphur salts*, H S + K S = K S, H S, — $Sb S_3$ + 3 Na S = 3 Na S, $Sb S_3$. The sulphur acids being weak acids, the soluble sulphur salts have all of them alkaline reaction.

a. OXYGEN ACIDS.

§ 22.

1. Sulphuric Acid (H O, $S O_3$).

We use—

a. Concentrated sulphuric acid of commerce, English oil of vitriol.

b. Concentrated pure sulphuric acid.

The surest plan of preparing pure and strong sulphuric acid is as follows:

Oil of vitriol is poured into 4 times its weight of water, and a slow stream of hydrosulphuric acid gas is passed through the mixture for some hours. The acid is now left at rest several days; the clear liquid is then poured off from the precipitated sulphur, sulphide of lead and sulphide of arsenic, and heated in a tubulated retort with the beak inclined upwards, and with open tubulure, until vapors of sulphuric acid escape with those of the water.

The acid so purified is fit for nearly all the purposes of chemical analysis; if it is wished, however, to free it also from non-volatile substances, it may be distilled from a luted non-tubulated retort resting on a reversed crucible cover, and heated directly over charcoal.

The neck of the retort must reach so far into the receiver that the acid distilling over drops directly into the body. Refrigeration of the receiver by means of water is unnecessary and even dangerous. To prevent the flask coming into direct contact with the hot neck of the retort, some asbestos in long fibres is wrapt round that part of the neck where such contact might be apprehended.

As soon as the drops in the retort neck become oily in consistence, the receiver is changed and the concentrated acid is collected by itself.

c. Dilute sulphuric acid. This is prepared by adding to 5 parts of water in a leaden or porcelain dish, gradually, and whilst

stirring, 1 part of concentrated sulphuric acid. The sulphate of lead which separates is allowed to subside, and the clear fluid finally decanted from the precipitate.

Tests.—Pure sulphuric acid must be colorless; when colorless solution of sulphate of protoxide of iron is poured upon it in a test tube, no red tint must mark the line of contact of the two fluids (nitric acid, hypo-nitric acid); when diluted with twenty parts of water, it must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (nitrous acid).

When mixed with pure zinc and water, it must yield hydrogen gas; which, on being passed through a red-hot tube, must not deposit the slightest trace of arsenic. It must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with four or five parts of spirit of wine (oxide of lead, sesquioxide of iron, lime). The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test tube. If the point of contact is marked by turbidity (chloride of lead), lead is present. (*Lowenthal.*)

Uses.—Sulphuric acid has for most bases a greater affinity than almost any other acid; it is therefore used principally for the liberation and expulsion of other acids, especially of phosphoric, boracic, hydrochloric, nitric, and acetic acids.

Several substances which cannot exist in an anhydrous state (*e. g.*, oxalic acid), are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is owing to the great affinity which sulphuric acid possesses for water. The nature of the decomposed body may in such cases be inferred from the liberated products of the decomposition. Sulphuric acid is also frequently used for the evolution of certain gases, more particularly of hydrogen, and hydrosulphuric acid. It serves also as a *special* reagent for the detection and precipitation of baryta, strontia, and lead. What kind of sulphuric acid is to be used, whether the pure, or the purified acid, or the ordinary acid of commerce, whether concentrated or dilute, depends upon what the circumstances in each case may require. It will, however, be found that the necessary directions on this point are generally given in the present work.

§ 23.

2. Nitric Acid (H O, N O_5).

Preparation.—*a.* Heat crude nitric acid of commerce, as free as possible from chlorine, and of a specific gravity of at least 1·31,* in a glass retort, to boiling, with addition of some nitrate of potassa; let the distillate run into a receiver kept cool, and try from time to

* A weaker acid will not suit this mode of preparation.

time whether it still continues to precipitate or trouble solution of nitrate of silver. As soon as this ceases to be the case, change the receiver, and distil until a trifling quantity only remains in the retort. Dilute the distillate with water until the specific gravity of the diluted acid is 1·2.

b. Dilute crude nitric acid of commerce of about 1·38 specific gravity, with two-fifths of its weight of water; add solution of nitrate of silver as long as a precipitate of chloride of silver continues to form, [and in considerable excess besides. *Mulder.*—The solution of a coin in the same acid may be economically employed instead of pure nitrate.] Let the precipitate subside out of access of light, decant the perfectly clear supernatant acid into a tubulated retort; add some nitrate of potassa, free from chlorine, and distil until only a small quantity remains, taking care to attend to the proper cooling of the fumes distilling over. Dilute the distillate, if necessary, with water until it has a specific gravity of 1·2.

Tests.—Pure nitric acid must be colorless, and leave no residue upon evaporation on platinum foil. Addition of solution of nitrate of silver, or of nitrate of baryta, must not cause the slightest turbidity in it. It is advisable to dilute the acid with water before adding the reagents, as otherwise nitrates may precipitate.

Uses.—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, &c. With metals, and sulphides of metals, the acid oxidizes the metal present first, at the expense of part of its own oxygen, and then dissolves the oxide, forming a nitrate. Most oxides are dissolved by nitric acid at once as nitrates; and so are also most of the insoluble salts with weaker acids, the latter being expelled in the process by the nitric acid. Nitric acid dissolves also salts with soluble, non-volatile acids, as *e. g.* phosphate of lime, with which it forms nitrate of lime and acid phosphate of lime. Nitric acid is used also as an oxidizing agent: for instance, to convert protoxide of iron into sesquioxide, protoxide of tin into binoxide, &c.

§ 24.

3. Acetic Acid ($H\,O, C_4 H_3 O = H\,O, \bar{A}$).

A highly concentrated acetic acid is not required in qualitative analytical processes; the common acetic acid of commerce, which contains 25 per cent. of anhydrous acid, and has a specific gravity of 1·04, answers the purpose.

Tests.—Pure acetic acid must leave no residue upon evaporation, and—after saturation with carbonate of soda—emit no empyreumatic odor. Hydrosulphuric acid, solution of nitrate of silver, and solution of nitrate of baryta must not impair the transparency

of the dilute acid, nor must sulphide of ammonium, after neutralization of the acid by oxide of ammonium. Solution of indigo must not lose its color, when heated with the acid.

If the acid is not pure, add some acetate of soda and redistil from a glass retort, not quite to dryness; if it contains sulphurous acid (in which case hydrosulphuric acid will produce a white turbidity in it), digest it first with some binoxide of lead or finely pulverized binoxide of manganese, and then distil with acetate of soda.

Uses.—Acetic acid possesses a greater solvent power for some substances than for others; it is used, therefore, to distinguish the former from the latter; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. Acetic acid is occasionally used also to acidulate fluids where it is wished to avoid the employment of mineral acids.

§ 25.

4. Tartaric Acid ($2\,H\,O, C_8\,H_4\,O_{10} = 2\,H\,O, \bar{T}$).

The tartaric acid of commerce is sufficiently pure for the purposes of chemical analysis. It is kept best in powder, as its solution suffers decomposition after a time, a white film forming upon its surface. For use, it is dissolved in a little water with the aid of heat.

Uses.—The addition of tartaric acid to solutions of sesquioxide of iron, protoxide of manganese, and various other oxides of metals, prevents the usual precipitation of these metals by an alkali; this non-precipitation is owing to the formation of double tartrates, which are not decomposed by alkalies.

Tartaric acid may therefore be employed to effect the separation of these metals from others, the precipitation of which it does not prevent. Tartaric acid forms a difficultly soluble salt with potassa, but not so with soda; it is, therefore, one of our best reagents to distinguish between the two alkalies.

The *bitartrate of soda* is even better adapted for the detection of potash than the free acid. It is prepared by dividing a solution of tartaric acid into two equal portions, neutralizing one with carbonate of soda (which is best done by adding solution of the latter to the boiling solution of the acid), adding the other portion of acid, and evaporating the solution to crystallization. For use, one part of the salt is dissolved in about 10 parts of water.

b. HYDROGEN ACIDS AND HALOGENS.

§ 26.

1. Hydrochloric Acid (H Cl).

Preparation.—Pour a cooled mixture of seven parts of concentrated sulphuric acid and two parts of water over four parts of

chloride of sodium in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath, until the evolution of gas ceases; conduct the evolved gas, by means of a double limbed tube, into a flask containing six parts of water, and take care to keep this vessel constantly cool. To prevent the gas from receding, the tube ought only to dip about one line into the water of the flask. When the operation is terminated, try the specific gravity of the acid produced, and dilute with water until it marks from 1·11 to 1·12. If you wish to ensure the absolute purity of the acid, and its perfect freedom from every trace of arsenic and chlorine, you must take care to free the sulphuric acid, intended to be used in the process, from arsenic and the oxygen compounds of nitrogen, according to the directions of § 22. A pure acid may also be prepared cheaply from the crude hydrochloric acid of commerce, by diluting the latter to a specific gravity of 1·12, and distilling the fluid, with addition of some chloride of sodium. If the crude acid contains chlorine, this should be removed first by the cautious addition of solution of sulphurous acid, before proceeding to the distillation; if, on the other hand, it contains sulphurous acid, this is removed in the same way by the cautious addition of some chlorine water.

Commercial hydrochloric acid not infrequently contains a very slight trace of chloride of arsenic, derived from arsenical oil of vitriol. To remove this, conduct into the acid a stream of hydrosulphuric acid, decant after standing for a day or two, from the deposited sulphur and sulphide of arsenic, and heat until all hydrosulphuric acid is expelled.

Tests.—Hydrochloric acid intended for the purposes of chemical analysis, must be perfectly colorless, and leave no residue upon evaporation. It must not impart a blue tint to a solution of iodide of potassium mixed with starch paste (chlorine), nor discolor a fluid made faintly blue with iodide of starch (sulphurous acid). Chloride of barium ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Hydrosulphuric acid must leave it unaltered. Sulphocyanide of potassium must not impart the least red tint to the diluted acid.

Uses.—Hydrochloric acid serves as a solvent for a great many substances. It dissolves many metals and sulphides of metals, forming chlorides, with evolution of hydrogen or of hydrosulphuric acid. It dissolves lower and higher oxides in the form of chlorides, the solution being, in the case of the higher oxides, mostly attended with liberation of chlorine. Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts with non-volatile and soluble acids, *apparently* without decomposing them (*e. g.*, phosphate of lime)

but the fact is that, in cases of this kind, a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed; thus, for instance, in the case of phosphate of lime, chloride of calcium and acid phosphate of lime are formed. With salts of acids forming no soluble acid compound with the base present, hydrochloric acid forms metallic chlorides, the liberated acids remaining free in solution (borate of lime). Hydrochloric acid is also applied as a *special* reagent for the detection and separation of oxide of silver, suboxide of mercury, and lead (see § 121); and likewise for the detection of free ammonia, with which it produces in the air dense white fumes of chloride of ammonium.

§ 27.

2. Chlorine (Cl) and Chlorine Water.

Preparation.—Mix 18 parts of common salt in coarse powder or crystals with 15 parts of *finely pulverized* good binoxide of manganese; put the mixture in a flask, pour a *completely cooled* mixture of 45 parts of concentrated sulphuric acid and 21 parts of water upon it, and shake the flask: a uniform and continuous evolution of chlorine gas will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. This method of *Wiggers* is excellent, and can be highly recommended. Conduct the chlorine gas evolved, first through a flask containing a little water, then into a bottle filled with cold water, and continue the process until the fluid is saturated. To procure a solution of chlorine entirely free from bromine, the wash-flask and receiving bottle must be changed when about half the gas has passed over. The last portion is pure. The chlorine water must be kept in a cellar, and carefully protected from the action of light; since, if this precaution is neglected, it speedily suffers complete decomposition, being converted into dilute hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle, protected from the influence of light by a case of pasteboard. Chlorine water which has lost its strong peculiar odor is unfit for use.

Uses.—Chlorine has a greater affinity than iodine and bromine for metals and for hydrogen. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Chlorine serves, moreover, to convert sulphurous acid into sulphuric acid, protoxide of iron into sesquoxide, &c.; and also to effect the destruction of organic substances, in presence of water, as it withdraws hydrogen from the latter, enabling thus the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For this latter purpose it is most advisable to *evolve* the chlorine in the fluid which contains the

organic substances; this is effected by adding hydrochloric acid to the fluid, heating the mixture to boiling, and then adding chlorate of potassa. This gives rise to the formation of chloride of potassium, water, free chlorine, and bichlorate of chlorous acid, which acts in a similar manner to chlorine.

§ 28.

3. NITRO-HYDROCHLORIC ACID. *Aqua regia.*

Preparation.—Mix one part of pure nitric acid with from three to four parts of pure hydrochloric acid.

Nitric acid and hydrochloric acid decompose each other, the decomposition resulting, in most cases, as *Gay-Lussac* has shown, in the formation of two compounds which are gaseous at the ordinary temperature, $N O_2 Cl_2$ and $N O_2 Cl$, and of free chlorine and water. If one equivalent of $N O_5$ is used to three equivalents of Cl H, it may be assumed that only chloro-hyponitric acid ($N O_2 Cl$), chlorine and water, are formed ($N O_5 + 3 H Cl = N O_2 Cl_2 + Cl + 3 H O$).

This decomposition occurs as soon as the fluid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the acids named, makes aqua regia our most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which metals are insoluble both in hydrochloric and in nitric acid; and also to decompose various metallic sulphides, *e. g.*, cinnabar, pyrites, &c.

§ 29.

4. HYDROFLUOSILICIC ACID (H Fl, $Si Fl_2$).

Preparation.—Take quartz sand, wash off every particle of dust, and dry thoroughly. Mix one part of the dry sand intimately with one part of perfectly dry fluor spar in powder; pour six parts of concentrated sulphuric acid over the mixture in a strong glass flask or in a non-tubulated retort, dry inside, and mix carefully by shaking the vessel. As the mixture swells up, when getting warm, it must at first fill the vessel only to one-third. The mouth of the flask or retort must be closed with a perforated cork, or a cap of india-rubber, into which one end of a somewhat wide glass tube, suitably bent at right angles, is fitted air-tight; the other limb reaching to the bottom of a tall flat-bottomed glass jar with just sufficient mercury to allow the end of the tube to dip into it to the extent of several lines; the mercury in the jar is covered with four

parts of water. Promote the disengagement of fluosilicic gas, which commences even in the cold, by exposing the flask or retort to a moderate heat in the sand-bath. Towards the end of the process a pretty strong heat should be applied. Every gas bubble ascending through the mercury produces in the water a precipitate of hydrated silicic acid. The rationale of this process is that, of every three equivalents of fluoride of silicon ($Si Fl_2$), one equivalent decomposes with two equivalents of water into silicic acid ($Si O_2$), which separates, and hydrofluoric acid, which combines with the two undecomposed equivalents of fluoride of silicon, forming hydrofluosilicic acid.

$$3 Si Fl_2 + 2 H O = 2 (H Fl, Si Fl_2) + Si O_2.$$

The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the exit tube must be placed under mercury, since it would speedily be choked if this precaution were neglected. The same end may be attained also by attaching a funnel to the exit tube, by means of vulcanized india-rubber, and letting the funnel alone dip into the water. It sometimes happens in the course, and especially towards the end of the operation, that the gas forms complete channels of silica in the gelatinous liquid, through which it gains the surface without undergoing decomposition, if the liquid is not occasionally stirred. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth, squeeze the fluid through, and filter it afterwards. Keep the filtrate for use.

Tests.—Hydrofluosilicic acid, mixed with two parts of water, must produce no precipitate in solutions of salts of strontia.

Uses.—Bases decompose with hydrofluosilicic acid, forming water and metallic silicofluorides. Many of these are insoluble, whilst others are soluble; the latter may therefore by means of this reagent be distinguished from the former. In the course of analysis, hydrofluosilicic acid is applied simply for the detection of baryta.

c. SULPHUR ACIDS.

§ 30.

5. Hydrosulphuric Acid (*Sulphuretted Hydrogen*) (H S).

Preparation.—Hydrosulphuric acid gas is evolved best from sulphide of iron, which is broken into small lumps, and then treated with dilute sulphuric acid. Fused sulphide of iron may be procured so cheaply in commerce that it is hardly worth while to take the trouble of preparing it expressly. It may, however, be made, if necessary, by heating iron turnings or nails, from 1 to 1½ inch long, in a Hessian crucible to a white heat, and then adding small lumps

of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this is the case, the fused mass is poured out on sand, or into an old Hessian crucible. By making a hole in the bottom of the crucible in which the mixture is fused, the sulphide of iron will, as fast as it forms, run through, and may be received in a coal-shovel placed in the ash-pit. Or, introduce an intimate mixture of thirty parts of iron filings and twenty-one parts of flowers of sulphur, gradually and in small portions at a time, into a red-hot crucible, awaiting always the incandescence of the portion last introduced, before proceeding to the addition of a fresh one. When the whole mixture has been brought into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to fuse the sulphide of iron.

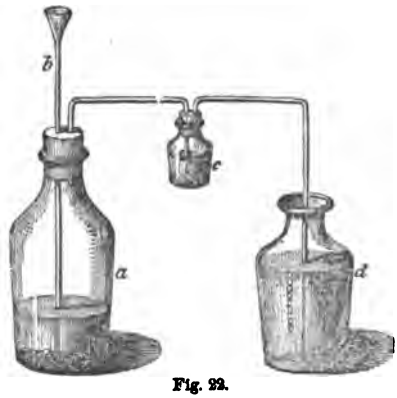


Fig. 22.

The evolution of the gas is effected in the apparatus illustrated by Fig. 22.

Pour water over the sulphide of iron in *a*, add concentrated sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, pour the fluid from off the still undecomposed sulphide of iron, wash the bottle repeatedly with water, fill it with that fluid, and keep it for the next operation. If you neglect this, the apparatus will speedily become incrusted with crystals of sulphate of protoxide of iron, which is apt to interfere injuriously with subsequent processes of evolution of gas.

For larger laboratories, or for chemists, having to operate often and largely with hydrosulphuric acid, I can recommend the lead apparatus designed by myself, which I have now for several years employed with the most satisfactory results in my own laboratory* (see Figs. 23 and 24).

a b c d and *e f g h* (Fig. 24) are two cylindrical leaden vessels, soldered with pure lead. They are both of the same size (in my own apparatus 13 inches high, and 12 inches in diameter). *i* is a false bottom of lead, perforated like a sieve, placed about 2 inches above the actual bottom of the vessel, and resting on leaden feet, which support it on the sides as well as also more particularly in

* The apparatus is made by *Mr. Stumpf*, of Wiesbaden, mechanist, and fully answers all reasonable demands, both as regards workmanship and price.

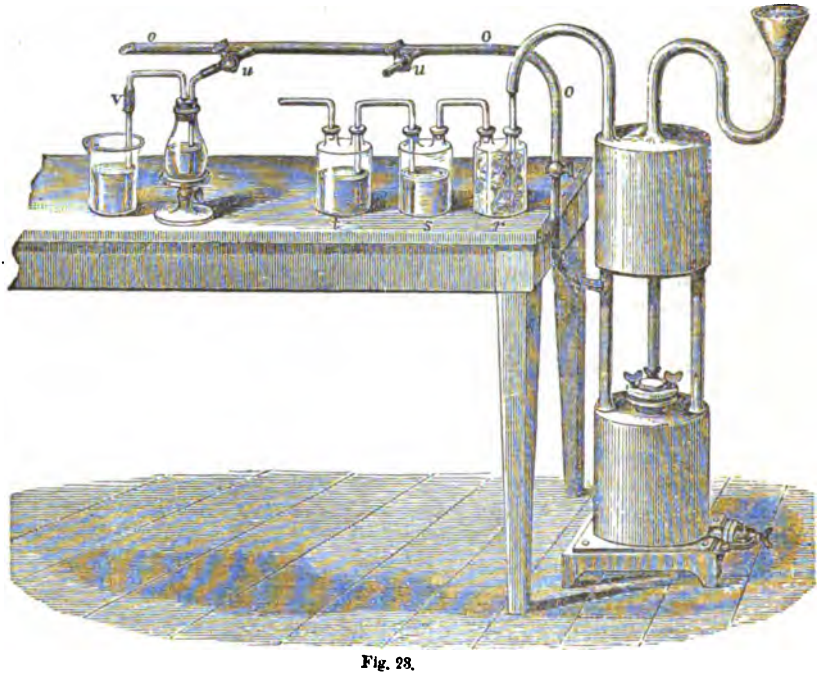


Fig. 23.

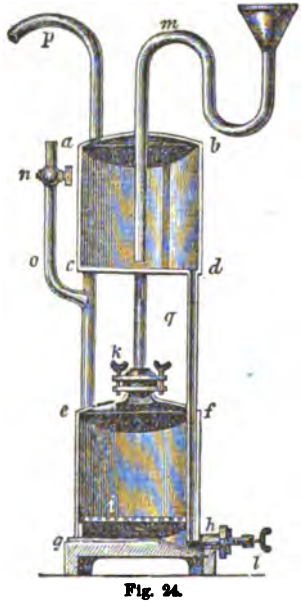


Fig. 24.

the middle. The numerous holes in the sieve-like bottom have a diameter of 0.06 of an inch; *k* shows the opening through which the sulphide of iron is introduced into the vessel. In my apparatus this aperture has a diameter of $2\frac{3}{4}$ inches, and is closed by putting a greased leather ring on its broad smooth rim, and pressing down upon this by means of three thumb-screws, the broad rim of the smooth turned cover. *l* shows the opening through which the solution of sulphate of protoxide of iron is drawn off; it will be seen by the drawing that the bottom of the vessel (*g h*) slants towards the part where this opening is placed. The aperture has a diameter of about $1\frac{1}{4}$ inches; it is closed by means of a smooth-turned broad and thick leaden cap, fitting on the smooth-turned broad rim, and pressed down upon it with a thumb-screw. The semi-

elliptical clamp which carries the female screw is movable, and hinged to the sides of *l* in a manner to admit of its being put out of reach of the liquid on drawing off the latter. The construction of the filling tube, *m*, may be learned from the drawing, and equally so that of the tube *d h*, which is intended to convey the acid from the upper to the lower vessel, and *vice versâ*. It will be seen from the drawing that this tube reaches down into the slanting and deepened part of the bottom *g h*, without, however, actually touching the latter. The tube *c e* is closed at the top, and has, therefore, no communication with the upper vessel, being simply intended to let off the gas evolved in *e f g h*; to which end it is connected laterally by a branch tube, with the tube *o*; this latter tube is fitted with a stop-cock (*n*). The tube *q* is closed at both ends, and serves simply as an additional support for the upper vessel. The tubes may have an inner diameter of half an inch.

The process of filling is conducted as follows: put 3·3 kilogrammes* of fused sulphide of iron, broken in lumps, through the mouth *k*, upon the perforated bottom *i*; screw the covers properly down upon *k* and *l*, shut the cock *n*, and pour through the funnel of *m* first 7 litres of water, then 1 litre of concentrated sulphuric acid, and then again 7 litres of water. The air in *a b c d* escapes in this operation through *p*, even when the latter tube is already connected with the flasks *r*, *s*, *t*.

If the cock *n* is now opened, and one of the cocks *u*, the acid will flow through the tube *d l* into *e f g h*; and through *o* air will escape at first, followed by the hydrosulphuric acid evolved in *e f g h*. As is seen in the figure, the tube *o* rises only to a certain elevation, when it makes a bend, running on thence in a horizontal direction. As many cocks, *u u*, are added as is thought desirable; these cocks are common brass gas stop-cocks, close-fitting and well ground in. They are connected with a small washing bottle; a double bent tube conveys the gas from the latter, with the co-operation of a straight tube connected with it by means of vulcanized india-rubber, into the fluid which it is intended to operate on; this arrangement greatly facilitates the cleansing of the straight tube dipping into the fluid. Upon now opening one of the cocks, *u*, the cock *n* being of course also open, you will at once obtain a current of gas of any strength desired, which will keep on for days in a continuous and steady stream. If all the cocks *u*, are shut, the gas evolved in *e f g h* forces the acid back to the upper vessel through the tube *h d*, and the evolution ceases.

The cessation of the evolution of gas is not instantaneous, however, as the sulphide of iron in *e f g h* remains still moistened with

* The quantities here given are calculated for an apparatus of the dimensions stated.

acid; moreover, small particles of the sulphides will always crumble off, and dropping through the sieve, come into contact with the rest of the acid covering the bottom, *g h*. Now the gas which still continues to be evolved in *e f g h*, being no longer able to escape through *o*, forces the fluid up *h d*, and passing through the acid in *a b c d*, makes its way out through *p*. To save this gas and keep it from poisoning the air, the flasks *r*, *s*, *t* are connected with *p*. *r* contains cotton, and serves the purpose of a washing bottle;* *s* and *t* contain solution of ammonia; but the two flasks together should contain no more than either of them can conveniently hold; since, as the pressure of the gas increases or relaxes, the fluid is forced from *s* to *t*, or back from *t* to *s*. It will be readily understood that sulphide of ammonium is formed in these flasks.

The evolution of gas ceases completely when all the acid is consumed, but there remains still the one half of the sulphide of iron, as the quantity used is calculated for double the amount of acid. The solution of sulphate of protoxide of iron is therefore drawn off, and 1 litre of acid and 14 of water again poured in as directed. This apparatus is now made also of much less dimensions to adapt it for smaller laboratories.

The apparatus described by *Pohl* deserves mention as being simple of construction and convenient in use. It is represented in Fig. 25. The bottle *A* containing the dilute sulphuric acid may contain from 1 to 3 or more quarts. In the caoutchouc stopper *B*, a stout glass-rod *G*, of at least $\frac{3}{8}$ of an inch in diameter, passes with considerable friction. Below, it bears a perforated basket, *K*, of hard rubber. It is lined with coarse linen and filled with lumps of fused sulphide of iron. When the glass-rod is so far depressed that the sulphide of iron just reaches the acid, a slow evolution of gas takes place. The flow of gas is increased by immersing the basket, or checked by raising it above the liquid. The wide tube *R*, which forms a part of the delivery tube, is filled loosely with cotton and perfectly serves the purpose of a wash-bottle.†

Fig. 25.

[In the Sheffield Laboratory of Yale College the supply of hydrosulphuric acid is obtained from two large self-regulating

* A common washing bottle filled with water could not well be used, as the water would very speedily recede.

[† This form of *Kemp's* gas generator is still more easily constructed by adopting

generators, like those commonly employed in the Döbereiner hydrogen lamp. To construct such a generator, procure a glass cylinder 8 or 9 inches in diameter, and 12 to 15 inches high, and a stout tubulated bell-glass 4 to 5 inches wide and 2 or 3 inches shorter than the cylinder. Procure also a basket of sheet-lead 3 inches deep, and an inch narrower than the bell-glass, whose sides and bottom are perforated with a number of small holes. Cast a circular plate of lead, of diameter 1½ inches larger than that of the cylinder and ¼ of an inch thick. On what is intended for its under side solder three equidistant leaden strips to keep the plate in proper position as a cover for the cylinder. Obtain a well-made brass gas-cock, fit to each end of it either by its screws or by soldering, a piece of brass or leaden tube 3 inches long, ½ to ¾ inches wide and stout in metal. Perforate the centre of the leaden plate, so that one of these tubes will snugly pass the orifice and secure it by solder, leaving 2 inches of the tube projecting below the plate. Attach a stout copper hook to the lower end of the tube by which to hang the leaden basket. By means of a good tightly fitting cork and cement, secure this tube into the neck of the bell-glass air-tight and so firmly that a weight of several pounds will not break the joining. Hang the basket, filled with lumps of fused sulphide of iron, within the bell and two inches above the bottom of the latter. To the tube, which extends above the stop-cock, attach, by a good cork, the neck of a 4 or 6 oz. tubulated globular receiver, which is to be loosely stuffed with cotton. To the tubulure of the receiver fit a tube bent at a right angle. On the depending arm of the latter tube is adapted, by a rubber connector, the wide tube which is to convey the gas into any solution. The cylinder is now filled with dilute sulphuric acid (1 vol. to 14 water) to within 1½ inches of the top, the bell-glass, full of air, being in its place. By opening the cock the air is expelled, and by the action of the acid upon the sulphide of iron the bell-glass is speedily filled with hydrosulphuric acid which replaces itself without any waste until either the acid is saturated or the sulphide of iron is dissolved. In cold weather this apparatus operates best when slightly warmed, especially if the acid be not fresh.]

Sulphuretted hydrogen water (*solution of hydrosulphuric acid*) is prepared by conducting the gas into very cold water, which has been previously freed from the air by boiling. The operation is continued until the water is completely saturated with the gas, which may be readily ascertained by closing the mouth of the flask

the following modifications. Instead of a glass rod, as above prescribed, a stout tube of the same diameter may be used. The basket is simply made of sheet-lead or of a bit of wide lead tubing, or even a linen bag will suffice. A good cork will take the place of the caoutchouc stopper, particularly if it be soaked for some time in melted tallow to fill up its pores.]

with the thumb, and shaking it a little: if, upon this, a pressure is felt from within, tending to push the thumb off the aperture of the flask, the operation may be considered at an end; but if, on the contrary, the thumb feels sucked into the mouth of the flask, this is a sure sign that the water is still capable of absorbing more gas.

Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer complete decomposition, the hydrogen being oxidized to water, and a small portion of the sulphur to sulphuric acid, the rest of the sulphur separating. The best way of preserving it unaltered for a very long time is to pour the freshly-prepared solution immediately into small phials, and to place the latter, carefully corked, in an inverted position, into bottles filled with water.

Tests.—Pure sulphuretted hydrogen water must be perfectly clear, and strongly emit the peculiar odor of the gas; when treated with sesquichloride of iron, it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it. It must leave no residue upon evaporation on platinum.

Uses.—Hydrosulphuric acid has a strong tendency to undergo decomposition with metallic oxides, forming water and metallic sulphides; and the latter, being mostly insoluble in water, are usually precipitated in the process. The conditions under which the precipitation of certain sulphides ensues differ materially; by altering or modifying these conditions, we may therefore divide the whole of the precipitable metals into groups, as will be found explained below. Hydrosulphuric acid is therefore an invaluable agent to effect the separation of metals into principal groups. Some of the precipitated sulphides exhibit a characteristic color indicative of the individual metals which they respectively contain. Hydrosulphuric acid serves thus more particularly for the *special* detection of tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information upon this point, I refer to the third section. The great facility with which hydrosulphuric acid is decomposed, renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce salts of sesquioxide of iron to salts of protoxide, chromic acid to the state of sesquioxide of chromium, &c. In these processes of reduction, the sulphur separates in the form of a fine white powder. Whether the hydrosulphuric acid had better be applied in the gaseous form, or in aqueous solution, depends always upon the special circumstances of the case.

III. BASES AND METALS.

§ 31.

Bases are divided into oxygen bases and sulphur bases. The former result from the combination of metals or of compound radi-

cals of similar character with oxygen, the latter from the combination of the same bodies with sulphur.

The *oxygen bases* are classified into alkalies, alkaline earths, earths proper, and oxides of the heavy metals. The alkalies are readily soluble in water; the alkaline earths dissolve with greater difficulty in that menstruum; and magnesia, the last member of the class, is only very sparingly soluble in it. The earths proper, and the oxides of the heavy metals are insoluble in water, or nearly so. The solutions of the alkalies and alkaline earths are caustic when sufficiently concentrated; they have an alkaline taste, change the yellow color of turmeric paper to brown, and restore the blue tint of reddened litmus paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colors, whilst those with weak acids generally have an alkaline reaction. The earths proper and the oxides of the heavy metals combine likewise with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The *sulphur bases* resulting from the combination of the metals of the alkalies and alkaline earths with sulphur, are soluble in water. The solutions have a strong alkaline reaction. The other sulphur bases do not dissolve in water. All sulphur bases form with sulphur acids *sulphur salts*.

a. OXYGEN BASES.

a. Alkalies.

§ 32.

1. Potassa (K O) and Soda (Na O).

The preparation of perfectly pure potassa or soda is a difficult operation. It is advisable, therefore, to prepare, besides perfectly pure caustic alkali, also some which is not quite pure, and some which, being free from certain impurities, may in many cases be safely substituted for the pure substance.

a. Common solution of soda.

Preparation.—Put into a clean cast-iron pan provided with a lid, 15 parts of crystallized carbonate of soda of commerce and 3 parts of water, heat to boiling, and add, in small portions at a time, milk of lime prepared by pouring 3 parts of warm water upon 1 part of quicklime, and letting the mixture stand in a covered vessel until the lime is reduced to a uniform pulpy mass. Keep the liquid in the pan boiling whilst adding the milk of lime, and for a quarter of an hour longer, then filter off a small portion, and try whether the filtrate still causes effervescence in hydrochloric acid. If this is the case, the boiling must be continued, and, if necessary, some more milk of lime added to the fluid. When

the solution is perfectly free from carbonic acid, cover the pan, allow the fluid to cool a little, and then draw off the clear solution from the residuary sediment, by means of a syphon filled with water, and transfer it to a glass flask. Boil the residue a second and a third time with water, and draw off the fluid in the same way. Cover the flask closely with a glass plate, and allow the lime suspended in the fluid to subside completely. Scour the iron pan clean, pour the clear solution back into it, and evaporate it to 6 or 7 parts. The solution so prepared has a sp. gr. of 1.13 to 1.15, and contains from 9 to 10 per cent. of soda. It must be clear, colorless, and as free as possible from carbonic acid; sulphide of ammonium must not impart a black color to it. Traces of silicic acid, alumina, and phosphoric acid, are usually found in a solution of soda prepared in this manner; on which account it is unfit for use in accurate experiments.

Solution of soda is kept best in bottles closed with ground glass caps. In default of capped bottles, common ones with ground stoppers may be used; but in that case, the neck must be wiped perfectly dry and clean inside, and a slip of writing paper rolled round the stopper; or, better, the stopper is smeared with a little paraffine before putting it into its place. If these precautions are neglected, it will be found impossible, after a time, to remove the stopper, particularly if the bottle is only rarely opened.

b. Hydrate of potassa purified with alcohol.

Preparation.—Dissolve some sticks of caustic potassa of commerce in rectified spirit of wine in a stoppered bottle, by digestion and shaking; let the fluid stand, decant or filter if necessary, and evaporate the clear fluid in a covered silver dish over the spirit-lamp, until no more aqueous vapors escape; adding from time to time, during the evaporation, some water, to prevent blackening of the mass. Place the silver dish in cold water until it has sufficiently cooled; remove the cake of caustic potassa from the dish, break it into coarse lumps in a hot mortar, and keep in a well-closed glass bottle. When required for use, dissolve some of it in water.

The hydrate of potassa so prepared is sufficiently pure for most purposes; it contains, indeed, a minute trace of alumina, but is usually free from phosphoric acid, sulphuric acid, and silicic acid. The solution must remain clear upon addition of sulphide of ammonium; hydrochloric acid must only produce a barely perceptible effervescence in it. The solution, acidified with hydrochloric acid, must, upon evaporation to dryness, leave a residue which dissolves in water to a clear fluid; when boiled with molybdate of ammonia, it must exhibit no yellow color; when treated with ammonia, it ought not to deposit slight flakes of alumina immediately; but only after standing several hours in a warm place.

c. Hydrate of potassa prepared with baryta.

Preparation.—Dissolve pure crystals of baryta (§ 34) by heating with water, and add to the solution pure sulphate of potassa, until a portion of the filtered fluid, acidified by hydrochloric acid and diluted, no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of sulphate of potassa). Let the turbid fluid clear, decant, and evaporate in a silver dish as in *b*. The hydrate of potassa so prepared is perfectly pure, except that it contains a trifling admixture of sulphate of potassa, which is left behind upon dissolving the hydrate in a little water. This hydrate is but rarely required, its use being in fact exclusively confined to the detection of minute traces of alumina.

Uses.—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect the decomposition of the salts of most bases, and consequently the precipitation of those bases which are insoluble in water. Many of the so precipitated oxides redissolve in an excess of the precipitant, as, for instance, alumina, sesquioxide of chromium, and oxide of lead; whilst others remain undissolved, *e. g.*, sesquioxide of iron, teroxide of bismuth, &c. The fixed alkalies serve therefore also as a means to separate the former from the latter. Potassa and soda dissolve also many salts (*e. g.*, chromate of lead), sulphur compounds, &c., and serve thus to separate and distinguish them from other substances. Many of the oxides precipitated by the action of potassa or soda exhibit a peculiar color, or possess other characteristic properties that may serve to lead to the detection of the individual metal which they respectively contain; such are, for instance, the precipitate of protoxide of manganese, hydrate of protoxide of iron, suboxide of mercury, &c. The fixed alkalies expel ammonia from its salts, and enable us thus to detect that body by its smell, its reaction on vegetable colors, &c.

§ 33.

2. Ammonia—*Oxide of Ammonium*—(NH_4O).

Preparation.—The apparatus illustrated by Fig. 22 (§ 30) may also serve for the preparation of solution of ammonia, with this modification, however, that no funnel tube being required in the process, the cork upon the flask *a* has only one perforation for the reception of the tube which serves to conduct the evolved ammonia into the washing bottle. Introduce into *a* 4 parts of chloride of ammonium in pieces about the size of a pea, and dry hydrate of lime prepared from 5 parts of lime; mix by shaking the flask, and add cautiously a sufficient quantity of water to make the powder into lumps. Put a small quantity of water only into the washing bottle (which should be rather capacious); but have 10 parts of

water in the flask which is intended for the final reception of the washed gas. Set the flask *a* now in a sand bath, connect it with the rest of the apparatus, place the flask *d* in a vessel of cold water, and apply heat. The evolution of gas speedily commences. Continue to heat until no more bubbles appear. Open the cork of the flask *a*, to prevent the receding of the fluid. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver *d* is perfectly pure; dilute it with water until the specific gravity is about 0·96=10 per cent. of ammonia. Keep the fluid in bottles closed with ground stoppers. This is the best way of preparing solution of ammonia in small quantities. That prepared on a large scale in cast-iron vessels is of course cheaper.

Tests.—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated on a watch-glass, nor should it cause the slightest turbidity in lime water (carbonic acid). [*Concentrated* ammonia precipitates lime-water though free from carbonic acid. It should, therefore, be diluted before testing.] When supersaturated with nitric acid, neither solution of nitrate of baryta, nor of nitrate of silver, must render it turbid, nor must sulphuretted hydrogen impart to it the slightest color.

Uses.—Solution of ammonia, although formed by conducting ammoniacal gas ($N H_3$) into water, and letting that gas escape upon exposure to the air, and much quicker when heated, is conveniently regarded as a solution of oxide of ammonium ($N H_4 O$) in water, the equivalent of water (H O) existing with $N H_3$ being assumed to form with the latter $N H_4 O$. Solution of ammonia is accordingly regarded as corresponding to the solution of potassa and soda, which greatly serves to facilitate the explanation of many chemical transformations into which the ammoniacal compounds enter, the oxygen salts resulting from the neutralization of oxygen acids by solution of ammonia being also assumed to contain oxide of ammonium $N H_4 O$, instead of N H. Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in an excess of ammonia, as, for instance, the oxides of zinc, cadmium, silver, copper, &c., whilst others are insoluble in free ammonia. This reagent may serve, therefore, to separate and distinguish the former from the latter. Some of these precipitates as well as their solutions in ammonia, exhibit peculiar colors, which may at once lead to the detection of the individual metal which they respectively contain.

Many of the oxides which are precipitated by ammonia from neutral solutions, are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the formation of a salt of ammonia. Compare § 54, chloride of ammonium.

β. ALKALINE EARTHS.

§ 34.

1. Baryta (Ba O).

Preparation.—a. From sulphate of baryta. Mix together 6 parts of finely pulverized sulphate of baryta, 1 part of powdered charcoal, and 1½ part of flour; or 8 parts of sulphate of baryta, 2 parts of charcoal, and 1 part of common resin. Put the mixture in a crucible, and expose it in a wind furnace to a long-continued red heat; or put the mixture in an earthen pot, lute the lid on with clay, and expose the pot to the heat of a brick-kiln. Boil the crude sulphide of barium obtained by this process for some time with water, and, when the crystallization point is attained, filter off hot: let the filtrate cool in a well-covered vessel. Pour off the mother liquor, which, together with the residue left from the boiling of the sulphide of barium, may be used for the preparation of chloride of barium; boil the crystals with just sufficient water to dissolve them; keep boiling (taking care to replace the evaporated water); add finely triturated and sifted copper scales in small portions at a time, until a filtered sample of the fluid gives a pure white precipitate when mixed with a little acetate of lead. Filter boiling. As solution of baryta eagerly absorbs carbonic acid from the air, great care must be taken to exclude the air in the process of filtration and crystallization. To effect this it is necessary to place the beaker intended to receive the filtrate on a flat dish or flat iron pot containing a little milk of lime, invert a bell-glass over it with an opening in the top, insert the funnel through this, filter, then remove the funnel, close the opening in the top of the bell-glass with an india-rubber cap, and let the fluid thus protected from access of air stand for several days in a cool place. After this decant the fluid (baryta water), let the crystals (Ba O, H O + 8 aq.) drain in a well-covered funnel, dry them quickly between sheets of blotting-paper, and keep them in well-stoppered bottles. For use dissolve 1 part in 20 parts of water, and filter. The baryta water so obtained is preferable to that decanted from the crystals.

b. From Witherite.—Mix intimately 100 parts of finely pulverized Witherite, 10 parts of powdered charcoal, and 5 parts of resin; or 100 parts of Witherite and 15 parts of finely powdered caking coal. Put the mixture in a pot or crucible, lute on the lid with clay, and expose to the heat of a brick-kiln. Triturate the mass, and boil the powder with water; filter, and proceed with the filtrate, as in *a*. The undissolved residue, which consists of undecomposed Witherite and coal, may be used in the preparation of chloride of barium. This is a most excellent method, both as regards cheapness and purity of product.

Tests.—Solution of baryta, or baryta water, must, after precipi-

tation of the baryta by sulphuric acid, give a filtrate remaining clear when mixed with spirit of wine, and leaving no fixed residue upon evaporation in a platinum crucible.

Uses.—Caustic baryta, being a strong base, precipitates the earths and metallic oxides insoluble in water from the solutions of their salts. In the course of analysis we use it simply to precipitate magnesia. Baryta water may also be used to precipitate those acids which form insoluble compounds with this base; it is applied with this view to effect the detection of carbonic acid, the removal of sulphuric acid, phosphoric acid, &c.

§ 35.

2. LIME (Ca O).

We use—

a. Hydrate of lime.

b. Lime water.

The former is obtained by slacking pure calcined lime in lumps, in a porcelain dish, with half its weight of water. Hydrate of lime must be kept in a well-stoppered bottle.

To prepare lime water, digest hydrate of lime for some time with cold distilled water, shaking the mixture occasionally; let the undissolved portion of lime subside, decant, and keep the clear fluid in a well-stoppered flask.

If hydrate of lime or lime water is required, entirely free from traces of alkalies which usually exist in limestones, the lime is washed several times with water before it or its solution is preserved.

Tests.—Lime water must impart a strongly-marked brown tint to turmeric paper, and give a considerable precipitate with carbonate of soda. It speedily loses these properties upon exposure to air, and is thereby rendered totally unfit for analytical purposes.

Uses.—Lime forms with many acids insoluble, with others soluble salts. Lime water may therefore serve to distinguish the former acids, which it precipitates from their solutions, from the latter, which it will of course fail to precipitate. Many of the precipitable acids are thrown down only under certain conditions, *e. g.*, on boiling (citric acid), which affords a ready means of distinguishing between them by altering these conditions. We use lime water in analysis principally to effect the detection of carbonic acid, and also to distinguish between citric acid and tartaric acid. Hydrate of lime is chiefly used to liberate ammonia from the salts of ammonia.

γ. HEAVY METALS AND THEIR OXIDES.

§ 36.

1. ZINC (Zn).

Select zinc of good quality, and, above all, perfectly free from arsenic. The method described, § 135, 10 will serve to detect the

presence of the slightest trace of this substance. Fuse the metal, and pour the fused mass in a thin unbroken stream into a large vessel with water. Should the zinc contain arsenic, it must be rejected, as no practicable process of purifying it is known.—(*Eliot* and *Storer*.)

Uses.—Zinc serves in qualitative analysis for the evolution of hydrogen, and also of arsenetted and antimonetted hydrogen gases (compare §§ 134, 10 and 135, 10); it is occasionally used also to precipitate some metals from their solutions; in which process the zinc simply displaces the other metal (Cu O, S O_3+Zn=Zn O, S O_3+Cu).

§ 37.

2. IRON (Fe).

Iron reduces many metals, and precipitates them from their solutions in the metallic state. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

§ 38.

3. COPPER (Cu).

We use copper exclusively to effect the reduction of mercury, which precipitates upon it as a white coating shining with silvery lustre when rubbed. A copper coin scoured with fine sand, or in fact any clean surface of copper, may be employed for this purpose.

§ 39.

4. HYDRATE OF TEROXIDE OF BISMUTH (Bi O_3, H O).*

Preparation.—Dissolve bismuth, freed from arsenic by fusion with *hepar sulphuris*, in dilute nitric acid; dilute the solution as much as is practicable without producing a permanent precipitate; filter, and evaporate the filtrate to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, and dry the white precipitate, and keep it for use.

Tests.—Hydrosulphuric acid must throw down from a solution of this reagent in dilute nitric acid, a precipitate insoluble in ammonia and sulphide of ammonium; and, accordingly, the fluid filtered off from the precipitate treated with ammonia must remain perfectly clear upon addition of hydrochloric acid, whilst in that

* The basic nitrate of teroxide of bismuth of commerce, if perfectly free from arsenic and antimony, may also be used instead of the hydrate of teroxide.

filtered off from the precipitate treated with sulphide of ammonium, that acid must only produce a pure white turbidity (sulphur).

Uses.—Teroxide of bismuth, when boiled with alkaline solutions of metallic sulphides, decomposes with the latter, giving rise to the formation of metallic oxides and sulphide of bismuth. It is better adapted to effect decompositions of this kind than oxide of copper, since it enables the operator to judge immediately upon the addition of a fresh portion whether the decomposition is complete or not. It has still another advantage over the oxide of copper, viz., it does not, like the latter, dissolve in the alkaline fluid in presence of organic substances; nor does it act as a reducing agent upon reducible oxygen compounds. We use it principally to convert tersulphide and pentasulphide of arsenic into arsenious and arsenic acids, for which purpose oxide of copper is altogether inapplicable, since it converts the arsenious acid immediately into arsenic acid, being itself reduced to the state of suboxide.

[§ 40.

5. BINOXIDE OF LEAD ($Pb O_2$).

Preparation.—Dissolve separately 4 parts of crystallized acetate of lead and 3 parts of crystallized carbonate of soda in hot water, and filter if needful; mix the solutions, and pass well-washed chlorine gas through the mixture until it has become dark-brown and all effervescence from escape of carbonic acid gas has ceased. Throw on a filter and wash with hot water until nitrate of silver no longer causes any turbidity in the washings. The contents of the filter are dried for use.— *Wöhler.*

Tests.—Binoxide of lead, when boiled with thrice its bulk of pure nitric acid for several minutes and allowed to settle, must not communicate the faintest red color to the acid (absence of manganese).

Uses.—This reagent serves to oxydize sesquioxide of chromium when in alkaline solution to chromic acid. It also is a most delicate and characteristic test for manganese.]

b. SULPHUR BASES.

§ 41.

1. SULPHIDE OF AMMONIUM ($N H_4 S$).

We use in analysis—

a. Colorless proto-sulphide of ammonium.

b. Yellow bi-, ter-, &c., sulphide of ammonium.

Preparation.—Transmit hydrosulphuric acid gas through 3 parts of solution of oxide of ammonium until no further absorption takes place; then add 2 parts more of the same solution of oxide of ammonium. The action of hydrosulphuric acid upon oxide of ammonium gives rise to the formation, first of $N H_5 S$ ($N H_4 O$

and H S=N H_4 S and H O), then of N H_4 S, H S; upon addition of the same quantity of solution of ammonia as has been saturated, the oxide of ammonium decomposes with the double sulphide of ammonium and hydrogen, or, as it is commonly called, the hydrosulphate of sulphide of ammonium, and simple or proto-sulphide of ammonium is formed (N H_4 S, H S+N H_4 O=2 (N H_4 S)+H O. The rule, however, is to add only two-thirds of the quantity of solution of ammonia, as it is better the preparation should contain a little hydrosulphate of sulphide of ammonium, than that free ammonia should be present. To employ, as has usually been the case hitherto, hydrosulphate of sulphide of ammonium instead of the simple proto-sulphide, is unnecessary, and simply tends to increase the smell of sulphuretted hydrogen in the laboratory, as the preparation allows that gas to escape when in contact with metallic sulphur acids.

Sulphide of ammonium should be kept in small well-stoppered bottles. It is colorless at first, and deposits no sulphur upon addition of acids. Upon exposure to the air, however, it acquires a yellow tint, owing to the formation of bisulphide of ammonium, which is attended also with formation of ammonia and water:

$$2\,(N\,H_4\,S)+O=N\,H_4\,S_2+N\,H_3+H\,O.$$

Continued action of the oxygen of the air upon the sulphide of ammonium tends at first to the formation of still higher sulphides; but afterwards the fluid deposits sulphur, and, in the end, there remains nothing in solution but pure ammonia, the whole of the sulphur having separated.

The sulphide of ammonium, which has turned yellow by exposure to the air, may be used for all purposes requiring the employment of yellow sulphide of ammonium: the yellow sulphide may also be expeditiously prepared by digesting the proto-sulphide with some sulphur. All kinds of yellow sulphide of ammonium deposit sulphur, and look turbid and milky on being mixed with acids.

Tests.—Sulphide of ammonium must strongly emit the odor peculiar to it; with acids it must evolve abundance of sulphuretted hydrogen; the evolution of gas may be attended by the separation of a pure white deposit, but no other precipitate must be formed. Upon evaporation and exposure to a red heat on a platinum dish, it must leave no residue. It must not precipitate, nor even render turbid, solution of magnesia or solution of lime (carbonate of ammonia or free ammonia).

Uses.—Sulphide of ammonium is one of the most frequently employed reagents. It serves (*a*) to effect the precipitation of those metals which hydrosulphuric acid fails to throw down from acid solutions, *e. g.* of iron, cobalt, &c. (N H_4 S+Fe O, S O_3=Fe S+

N H, O, S O_3), (*b*) to separate the metallic sulphides thrown down from acid solutions by hydrosulphuric acid, as it dissolves some of them to sulphur salts, as, for instance, the sulphides of arsenic and antimony, &c. (N H, S, As S_3, &c.), whilst leaving others undissolved—for instance, sulphide of lead, sulphide of cadmium, &c. The sulphide of ammonium used for this purpose must contain an excess of sulphur, if the metallic sulphides to be dissolved will dissolve only as higher sulphides, as, for instance, Sn S, which dissolves with ease only as Sn S_2.

From solutions of salts of alumina and sesquioxide of chromium, sulphide of ammonium precipitates hydrates of these oxides, with escape of sulphuretted hydrogen, as the sulphur compounds corresponding to these oxides cannot form in the humid way. Al_2O_3, $3\,S\,O_3+3\,N\,H_4\,S+3\,H\,O=Al_2\,O_3,\,3\,H\,O+3\,(N\,H_4\,O,\,S\,O)+3\,H\,S$. Salts insoluble in water are thrown down by sulphide of ammonium unaltered from their solutions in acids; thus, for instance, phosphate of lime is precipitated unaltered from its solution in hydrochloric acid.

§ 42.

2. Sulphide of Sodium (Na S).

Preparation.—Same as sulphide of ammonium, except that solution of soda is substituted for solution of ammonia. Keep the fluid obtained in well-stoppered bottles. If required to contain some higher sulphide of sodium, digest it with powdered sulphur.

Uses.—Sulphide of sodium is substituted for sulphide of ammonium to effect the separation of sulphide of copper from sulphur compounds soluble in alkaline sulphides, *e. g.*, from proto-sulphide of tin, as sulphide of copper is not quite insoluble in sulphide of ammonium.

IV. SALTS.

Of the many salts employed as reagents, those of potassa, soda, and ammonia are used principally on account of their acids; salts of soda may, therefore, often be substituted for the corresponding potassa salts, &c. Thus it is almost always a matter of perfect indifference whether we use carbonate of soda or carbonate of potassa, ferrocyanide of potassium or ferrocyanide of sodium, &c. I have, accordingly, here classified the salts of the alkalies *by their acids*. With the salts of the alkaline earths and those of the oxides of the heavy metals the case is different; these are not used for their acid, but for their base; we may, therefore, often substitute for one salt of a base another similar one, as *e. g.*, nitrate or acetate of baryta for chloride of barium, &c. For this reason I have classified the salts of the alkaline earths and of the heavy metals *by their bases.*

a. SALTS OF THE ALKALIES.

§ 43.

1. Sulphate of Potassa (K O, S O_3).

Preparation.—Purify sulphate of potassa of commerce by recrystallization, and dissolve 1 part of the pure salt in 12 parts of water.

Uses.—Sulphate of potassa serves to detect and separate baryta and strontia. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 44.

2. Phosphate of Soda (2 Na O, H O, P O_5+24 aq.).

Preparation.—Purify phosphate of soda of commerce by recrystallization, and dissolve one part of the pure salt in 10 parts of water for use.

Tests.—Solution of phosphate of soda must not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it, must completely, and without effervescence, redissolve upon addition of dilute nitric acid.

Uses.—Phosphate of soda precipitates the alkaline earths, and all metallic oxides, by double affinity. It serves, in the course of analysis, after the separation of the oxides of the heavy metals, as a test for alkaline earths in general; and, after the separation of baryta, strontia, and lime, as a special test for the detection of magnesia; for which latter purpose it is used in conjunction with ammonia, the magnesia precipitating, under these circumstances, as basic phosphate of magnesia and ammonia.

§ 45.

3. Oxalate of Ammonia (2 N H_4 O, C_4 O_6+2 aq.).

Preparation.—Dissolve commercial oxalic acid which has been purified by recrystallization, in 2 parts of hot water, add caustic ammonia, or carbonate of ammonia, until the fluid begins to manifest a slight alkaline reaction; filter, and set aside to cool. The crystals that separate are allowed to drain, and the mother liquors are further evaporated to crystallization. Purify by recrystallization. Dissolve 1 part of the pure salt in 24 parts of water for use.

Tests.—The solution of oxalate of ammonia must not be precipitated nor rendered turbid by hydrosulphuric acid, nor by sulphide of ammonium. The salt must leave no residue after ignition on platinum foil.

Uses.—Oxalic acid forms with lime, strontia, baryta, oxide of lead, and other metallic oxides, insoluble or very difficultly soluble

compounds; oxalate of ammonia produces, therefore, in the aqueous solutions of the salts of these bases, precipitates of the corresponding oxalates. In analysis it serves principally for the detection of lime.

§ 46.

4. ACETATE OF SODA (Na O, $C_4 H_3 O_3$+6 aq., or Na O, $\bar{A}$+6 aq.).

Preparation.—Dissolve crystallized carbonate of soda in a little water, add to the solution acetic acid to slight excess, evaporate to crystallization, and purify the salt by recrystallization. For use dissolve 1 part of the salt in 10 parts of water.

Tests.—Acetate of soda must be colorless and free from empyreumatic matters and inorganic acids.

Uses.—The stronger acids in the free state decompose acetate of soda, combining with the base, and setting the acetic acid free. In the course of analysis, acetate of soda is used principally to precipitate phosphate of sesquioxide of iron (which is insoluble in acetic acid) from its solution in hydrochloric acid.

§ 47.

5. CARBONATE OF SODA (Na O, C O_2+10 aq.).

Preparation.—Finely pulverize bicarbonate of soda of commerce, put the powder into a funnel stopped loosely with some cotton, make the surface even, cover it with a disc of difficultly permeable paper with turned-up edges, and wash by pouring small quantities of water on the paper disc, until the filtrate, when acidified with nitric acid, is not rendered turbid by solution of nitrate of silver, nor by solution of chloride of barium. Let the salt dry, and then convert it by gentle ignition into the simple carbonate. This is effected best in a crucible or dish of silver or platinum; but it may be done also in a perfectly clean vessel of cast iron, or, on a small scale, in a porcelain dish. Pure carbonate of soda may be obtained also by repeated recrystallization of carbonate of soda of commerce. For use, dissolve 1 part of the anhydrous salt or 2·7 parts of the crystallized salt in 5 parts of water.

Tests.—Carbonate of soda intended for analytical purposes must be perfectly white. Its solution, when supersaturated with nitric acid, must not be rendered turbid by chloride of barium nor by nitrate of silver; nor must addition of sulphocyanide of potassium impart a red, or warming with molybdate of ammonia and nitric acid a yellow tint to it; the residue which remains upon evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, must leave no residue (silicic acid) when redissolved in water.

Uses.—With the exception of the alkalies, carbonate of soda

precipitates the whole of the bases, most of them as carbonates, but some also as hydrated oxides. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of soda exhibit a characteristic color, which may lead to the detection of the individual metals which they respectively contain. Solution of carbonate of soda serves, moreover, for the decomposition of many insoluble salts of the alkaline earths or of the metals, more particularly of those with organic acids. Upon boiling with carbonate of soda, these salts are converted into insoluble carbonates, whilst the acids combine with the soda, and are thus obtained in solution in the form of salts of soda. Carbonate of soda is often used also to saturate free acids.

§ 48.

6. Carbonate of Ammonia ($N H_4 O, C O_2$).

Preparation.—We use for the purpose of chemical analysis purified sesquicarbonate of ammonia, entirely free from any smell of animal oil, such as is prepared on a large scale from chloride of ammonium and carbonate of lime by sublimation. The outer and the inner surface of the mass are carefully scraped. One part of the salt is dissolved by digestion with 4 parts of water, to which one part of solution of caustic ammonia has been added.

Tests.—Pure carbonate of ammonia must completely volatilize. Neither solution of nitrate of baryta nor nitrate of silver, nor sulphuretted hydrogen, must color or precipitate it, after supersaturation with nitric acid.

Uses.—Carbonate of ammonia precipitates, like carbonate of soda, most metallic oxides and earths; it is generally employed in preference to the latter reagent, because it introduces no non-volatile body into the solution. Complete precipitation of many of the oxides takes place only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides and metallic sulphides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions many oxides which it precipitates from neutral solutions. (Compare § 54.) We use carbonate of ammonia in chemical analysis principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia, as the latter is not precipitated by this reagent in the presence of salts of ammonia.

§ 49.

7. Bisulphite of Soda ($Na\ O, 2\ S\ O_2$).

Preparation.—Heat 5 parts of copper shreds with 20 parts of concentrated sulphuric acid in a flask, and conduct the sulphurous acid gas evolved, first through a washing bottle containing some water, then into a flask containing 4 parts of purified bicarbonate of soda (§ 47), or 7 parts of crystallized carbonate of soda, and from 20 to 30 parts of water, and which is not much more than half full; continue the transmission of the gas until the evolution of carbonic acid ceases. Keep the solution, which smells strongly of sulphurous acid, in a well-stoppered bottle.

Tests.—Sulphite of soda, when evaporated to dryness with pure sulphuric acid must leave a residue,* the aqueous solution of which is not altered by hydrosulphuric acid, nor colored yellow by heating with a solution of molybdate of ammonia mixed with nitric acid.

Uses.—Sulphurous acid has a great tendency to pass to the state of sulphuric acid by absorbing oxygen. It is therefore one of our most powerful reducing agents. Sulphite of soda, which has the advantage of keeping better than sulphurous acid, acts in an analogous manner as a reducing agent upon acids and higher oxides. We employ it principally to reduce arsenic acid to arsenious acid, chromic acid to sesquioxide of chromium, and sesquioxide of iron to protoxide. It is besides employed for separating tersulphide of arsenic from the sulphides of antimony and tin; the former being soluble, the latter insoluble in solution of this reagent.

§ 50.

8. Nitrite of Potassa ($K\ O, N\ O_3$).

Preparation.—Heat 2 parts of starch in lumps, with 8 parts of crude nitric acid, sp. gr. 1.4, and 8 parts of water in a flask that is but half filled with the mixture, and conduct the nitrous vapors first through a large empty bottle, then into a flask containing 5 parts of potassa-ley of sp. gr. 1.27, until the latter is saturated, as is evinced by the separation of alumina or silica when common potassa is used. As soon as the evolution of gas begins, the heat must be removed for a while, as otherwise the action becomes too violent. The filtered solution is evaporated to dryness. When needed for use, dissolve 1 part of the solid salt in about 2 parts of water.

Tests.—Nitrite of potassa must, upon addition of dilute sulphuric acid, copiously evolve nitric oxide gas.

Uses.—Nitrite of potassa is an excellent means to effect the

* The evaporation is attended with copious evolution of sulphurous acid.

detection and separation of cobalt; in the solutions of which metal it produces a precipitate of nitrite of potassa and sesquioxide of cobalt. It serves also in presence of free acid to liberate iodine from its compounds.

§ 51.

9. BICHROMATE OF POTASSA (K O, 2 Cr O_3).

Preparation.—Purify the salt of commerce by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

Uses.—Chromate of potassa decomposes most of the soluble salts of metallic oxides, by double affinity. Most of the precipitated chromates are very difficultly soluble, and many of them exhibit characteristic colors which lead readily to the detection of the particular metal which they respectively contain. We use bichromate of potassa principally as a test for lead.

§ 52.

10. GRANULAR ANTIMONATE OF POTASSA (K O, Sb O_5+7 aq.).

A mixture of equal parts of pulverized tartar emetic and nitrate of potassa is projected little by little into a red-hot crucible. The mass is kept gently ignited for ¼ of an hour after the deflagration is finished; it foams somewhat at first, but afterwards enters into calm fusion. The crucible is allowed to cool and the whole is treated with warm water. The contents are thus easily removed, and the liquid deposits a heavy white powder from which it is decanted. The liquid itself is concentrated by evaporation. After 1 to 2 days a doughy mass separates. This is stirred by means of a spatula with thrice its volume of cold water, until it is converted into a fine granular powder, which is united with that first obtained. The whole is then washed with a little cold water and dried upon blotting paper. 100 parts of tartar emetic yield about 36 parts of antimonate of potassa. (*Brunner.*)

Tests and Uses.—Granular antimonate of potassa is quite difficultly soluble in water; it requires 90 parts of boiling and 250 parts of cold water for solution. The solution is best made just before use, by continued shaking of the pulverized salt with cold water and filtering off from the undissolved portion. The solution thus procured must be clear and have a neutral reaction; it must not be altered by solutions of chloride of potassium or chloride of ammonium, but must yield with chloride of sodium a crystallized precipitate. Antimonate of potassa is an excellent reagent for soda, but must be employed with much caution. Compare § 93.

§ 53.

11. Molybdate of Ammonia ($N H_4 O, Mo O_3$).

Preparation.—Triturate sulphide of molybdenum with an equal bulk of coarse quartz sand washed with hydrochloric acid, until the mass is reduced to a moderately fine powder; heat the powder to feeble redness, until the mass has acquired a lemon-yellow color (which after cooling turns whitish). With small quantities, this operation may be conducted in a flat platinum dish, with large quantities, in a muffle; take care to stir the mixture repeatedly during the operation. After cooling, digest the impure molybdic acid thus produced with solution of ammonia, filter, evaporate the filtrate to dryness, ignite the residue gently until the mass has become yellow or white, and digest this for some days in the water-bath with nitric acid in order to convert any phosphoric acid into the tribasic modification. After the nitric acid is evaporated, dissolve the residue in 4 parts of solution of ammonia, filter rapidly and pour the solution into 15 parts by weight of nitric acid of sp. gr. 1.20. Allow the solution to stand several days in a warm place until any phospho-molybdate of ammonia that may be present has separated, pour off the colorless solution from the precipitate, and keep for use. When heated to 104° Fah. the solution is unaltered; at a higher temperature a white precipitate of molybdic acid or acid molybdate of ammonia deposits, unless more nitric or hydrochloric acid be added. (*Eggertz.*)

Uses.—Phosphoric and arsenic acids form, with molybdic acid and ammonia, peculiar compounds of a yellow color, which are insoluble in a nitric acid solution of molybdate of ammonia. This reagent is therefore especially adapted for detecting minute traces of these acids in acid solutions containing oxide of iron, alumina, and alkaline earths.

§ 54.

12. Chloride of Ammonium ($N H_4 Cl$).

Preparation.—Select sublimed white sal-ammoniac of commerce. If it contains iron, it must be purified. [This is most readily accomplished by slowly passing chlorine gas into the nearly saturated solution *for a short time*, or until ferricyanide of potassium gives no blue color with a few drops of the liquid. Ammonia is then added in slight excess, the whole is warmed, filtered from the separated sesquioxide of iron, and evaporated to crystallization. Care must be taken not to allow chlorine to react too long or in too large quantity on the sal ammoniac, else chloride of nitrogen might be formed which is dangerously explosive.] For use, dissolve one part of the salt in 8 parts of water.

Tests.—Solution of chloride of ammonium must upon evapora-

tion on a platinum knife leave a residue which volatilizes completely upon continued application of heat. Sulphide of ammonium must leave it unaltered. Its reaction must be perfectly neutral.

Uses.—Chloride of ammonium serves principally to retain in solution certain oxides (*e. g.*, protoxide of manganese, magnesia) or salts (*e. g.*, tartrate of lime), upon the precipitation of other oxides or salts by ammonia or some other reagent. This application of chloride of ammonium is based upon the tendency of the ammonia salts to form double compounds with other salts. Chloride of ammonium serves also to distinguish between precipitates possessed of similar properties; for instance, to distinguish the *basic phosphate of magnesia and ammonia*, which is insoluble in chloride of ammonium, from other precipitates of magnesia. It is used also to precipitate from their solutions in potassa various substances which are soluble in that alkali, but insoluble in ammonia; *e. g.*, alumina, sesquioxide of chromium, &c. In this process the elements of the chloride of ammonium transpose with those of the potassa, and chloride of potassium, water, and ammonia are formed. Chloride of ammonium is applied also as a *special* reagent to effect the precipitation of platinum as ammonio-bichloride of platinum.

§ 55.

13. Cyanide of Potassium (K Cy).

Preparation.—Heat ferrocyanide of potassium of commerce (perfectly free from sulphate of potassa) gently, with stirring, until the crystallization water is completely expelled; triturate the anhydrous mass, and mix 8 parts of the dry powder with 3 parts of perfectly dry carbonate of potassa; fuse the mixture in a covered Hessian, or, better still, in a covered iron crucible until the mass is in a faint glow, and appears clear, and a sample of it, taken out with an iron spatula, looks perfectly white. Remove the crucible now from the fire, tap it gently, and let it cool a little until the evolution of gas has ceased; pour the fused cyanide of potassium into a heated crucible-shaped vessel of clean scoured iron or silver, or into a moderately hot Hessian crucible, with proper care to prevent the running out of any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible. Let the mass now slowly cool in a somewhat warm place. The cyanide of potassium so prepared is exceedingly well adapted for analytical purposes, although it contains carbonate and cyanate of potassa; which latter is upon solution in water transformed into carbonate of ammonia and carbonate of potassa ($K O, C N O + 4 H O = K O, C O_2 + N H_4 O, C O_2$). Keep it in the solid form in a well-stoppered bottle, and for use dissolve 1 part in 4 parts of distilled water, without application of heat.

[This salt occurs sufficiently pure for analytical purposes in commerce.]

Tests.—Cyanide of potassium must be of a milk-white color, and quite free from particles of iron or charcoal. It must completely dissolve in water to a clear fluid. It must contain neither silicic acid nor sulphide of potassium; the precipitate which salts of lead produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid, whereby hydrocyanic acid escapes, must completely dissolve in water to a clear fluid.

Uses.—Cyanide of potassium prepared in the manner described produces in the solutions of most of the salts with metallic oxides, precipitates of cyanides of metals or of oxides or carbonates, which are insoluble in water. The precipitated cyanides are soluble in cyanide of potassium, and may therefore be separated from the oxides or carbonates which are insoluble in cyanide of potassium, by further addition of the reagent. Some of the metallic cyanides redissolve in the cyanide of potassium, even in presence of free hydrocyanic acid and upon boiling, invariably as double cyanides; whilst others combine with cyanogen, forming new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are cobalticyanide of potassium, and ferro- and ferricyanide of potassium. These differ from the double cyanides of the other descriptions particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may accordingly serve also to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in cyanide of potassium. In the course of analysis, this reagent serves to effect the separation of cobalt from nickel, and also of copper whose sulphide it dissolves, from cadmium whose sulphide is insoluble.

§ 56.

14. Ferrocyanide of Potassium ($2\,K, C_3 N_3 Fe + 3\,aq. = 2\,K, Cfy + 3\,aq.$).

Preparation.—The ferrocyanide of potassium is found in commerce sufficiently pure for the purposes of chemical analysis. 1 part of the salt is dissolved in 12 parts of water for use.

Uses.—Ferrocyanogen forms with most metals compounds insoluble in water, and which frequently exhibit highly characteristic colors. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing places with the metals. Ferrocyanide of copper and ferrosesquicyanide of iron

exhibit the most characteristic colors of all; ferrocyanide of potassium serves therefore particularly as a test for oxide of copper and sesquioxide of iron.

§ 57.

15. FERRICYANIDE OF POTASSIUM (3 K, C_{12} N_6 Fe_2 = 3 K Cfdy).

Preparation.—Conduct chlorine gas slowly into a solution of 1 part of ferrocyanide of potassium in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep red color by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate, in a solution of sesquichloride of iron, but imparts a brownish tint to it; evaporate the fluid now in a dish to ¼ of its weight, and crystallize. The mother liquor will upon further evaporation yield a second crop of crystals equally fit for use as the first. Dissolve the whole of the crystals obtained in 3 parts of water, filter, if necessary; evaporate the solution briskly to half its volume, and crystallize again. Dissolve 1 part of the crystals, which are of a splendid red color, in 10 parts of water for use. The solution, as already remarked, must produce neither a blue precipitate nor a blue color in a solution of sesquichloride of iron. [The commercial salt is suited for all analytical purposes. This salt undergoes decomposition when long kept in solution. It is therefore best applied in the state of a fine powder.]

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, the ferriprotocyanide of iron is more particularly characterized by its color, and we apply ferricyanide of potassium therefore principally as a test for protoxide of iron.

§ 58.

16. SULPHOCYANIDE OF POTASSIUM (K, C_2 N S_2 or K, Cy S_2).

Preparation.—Mix together 46 parts of anhydrous ferrocyanide of potassium, 17 parts of carbonate of potassa, and 32 parts of sulphur; introduce the mixture into an iron pan provided with a lid, and fuse at a gentle heat; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; increase the temperature now, towards the end of the operation, to dull redness, in order to decompose the hyposulphite of potassa which has been formed in this process. Remove the half refrigerated and still soft mass from the pan, pulverize it, and boil with alcohol. Let the alcoholic solution cool, when part of the sulphocyanide of potassium will separate in colorless crystals; to obtain the remainder, distil the alcohol from the mother-liquor. Dissolve 1 part of the salt in 10 parts of water for use.

Uses.—Sulphocyanide of potassium serves for the detection of sesquioxide of iron; it is for that substance at once the most characteristic and delicate test. Its solution must remain colorless when heated with pure and dilute hydrochloric acid.

b. SALTS OF THE ALKALINE EARTHS.

§ 59.

Chloride of Barium (Ba Cl + 2 aq.).

Preparation.—a. From heavy spar. Triturate crude sulphide of barium (§ 34), boil about $\frac{9}{10}$ of the powder with 4 times the quantity of water, and add hydrochloric acid until all effervescence of sulphuretted hydrogen has ceased, and the fluid manifests a feeble acid reaction; add now the remaining $\frac{1}{10}$ part of the sulphide of barium, boil for some time longer, then filter, and let the alkaline fluid crystallize. Dry the crystals, redissolve them in water, and crystallize again.

b. From Witherite. Pour 10 parts of water upon 1 part of Witherite, and gradually add crude hydrochloric acid until the Witherite is almost completely dissolved. Add now a little more finely pulverized Witherite, and heat, with frequent stirring, until the fluid has entirely or very nearly lost its acid reaction; add some baryta water or solution of sulphide of barium, as long as a precipitate forms; filter, evaporate to crystallization; dry the crystals, redissolve them in water, and crystallize again. For use, dissolve 1 part of the chloride of barium obtained in 10 parts of water.

Tests.—Pure chloride of barium must not alter vegetable colors; its solution must not be colored or precipitated by hydrosulphuric acid, nor by sulphide of ammonium. Pure sulphuric acid must precipitate every fixed particle from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent leaves not the slightest residue when evaporated on platinum foil.

Uses.—Baryta forms with many acids soluble, with others insoluble compounds. This property of baryta affords us, therefore, a means of distinguishing the former acids which are not precipitated by chloride of barium from the latter, in the solution of the salts of which this reagent produces a precipitate. The precipitated salts of baryta severally show with other bodies (acids) a different deportment. By subjecting these salts to the action of such bodies, we are therefore enabled to subdivide the group of precipitable acids, and even to detect certain individual acids. This makes chloride of barium one of our most important reagents to distinguish between certain groups of acids, and more especially also for the detection of sulphuric acid.

§ 60.

2. NITRATE OF BARYTA (Ba O, N O_5).

Preparation.—Pour 12 parts of water upon 1 part of carbonate of baryta, no matter whether Witherite or precipitated by carbonate of soda from solution of sulphide of barium, gradually add dilute nitric acid free from chlorine, and proceed exactly as directed in the preparation of chloride of barium from Witherite. For use, dissolve 1 part of the salt in 15 parts of water.

Tests.—Solution of nitrate of baryta must not be made turbid by solution of nitrate of silver. Other tests the same as for chloride of barium.

Uses.—Nitrate of baryta is used instead of chloride of barium in cases where it is necessary to avoid the presence of a metallic chloride in the fluid.

§ 61.

3. CARBONATE OF BARYTA (Ba O, C O_2).

Preparation.—Dissolve crystallized chloride of barium in water, heat to boiling, and add a solution of carbonate of ammonia mixed with some caustic ammonia, or of pure carbonate of soda, as long as a precipitate forms; let it subside, decant five or six times, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of nitrate of silver. Stir the precipitate with water to the consistence of thick milk, and keep this mixture in a stoppered bottle. It must of course be shaken every time it is required for use.

Tests.—Pure sulphuric acid must precipitate every fixed particle from a solution of carbonate of baryta in hydrochloric acid (compare caustic baryta).

Uses.—Carbonate of baryta completely decomposes the solutions of many metallic oxides, *e. g.*, sesquioxide of iron, alumina; precipitating from them the whole of the oxide as hydrate and basic salt, whilst some other metallic salts are not precipitated by it. It serves therefore to separate the former from the latter, and is an excellent means to effect the separation of sesquioxide of iron and alumina from protoxide of manganese, oxide of zinc, &c., and also from lime and magnesia. For this purpose it must be remembered that the sulphates cannot be employed, as from them it throws down all the bases above mentioned.

§ 62.

4. SULPHATE OF LIME (Ca O, S O_3, crystallized Ca O, S O_3+2 aq.).

Preparation.—Digest and shake powdered crystallized gypsum for some time with water; let the undissolved portion subside, decant, and keep the clear fluid for use.

Uses.—Sulphate of lime being a difficultly soluble salt, is a convenient agent in cases where it is wished to apply a solution of a lime salt or of a sulphate of a definite degree of dilution. As dilute solution of a lime salt, it is used for the detection of oxalic acid; whilst as dilute solution of a sulphate it affords an excellent means of distinguishing between baryta, strontia, and lime.

§ 63.

5. CHLORIDE OF CALCIUM (Ca Cl, crystallized Ca Cl+6 aq.).

Preparation.—Dilute 1 part of crude hydrochloric acid with 6 parts of water, and add to the fluid marble or chalk until the last portion added remains undissolved; add some hydrate of lime, and then solution of hydrosulphuric acid until a filtered sample is not affected by sulphide of ammonium. Let it stand 12 hours at a gentle heat in a closed vessel; filter, exactly neutralize the filtrate, concentrate by evaporation, and crystallize. Let the crystals drain, and dissolve 1 part of the salt in 5 parts of water for use.

Tests.—Solution of chloride of calcium must be perfectly neutral, and neither be colored nor precipitated by sulphide of ammonium; nor ought it to evolve ammonia when mixed with hydrate of potassa or hydrate of lime.

Uses.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter reagent is used to divide the *inorganic* acids into groups, so chloride of calcium serves in the same manner to effect the separation of the *organic* acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others. And, as is the case with the baryta precipitates, the different conditions under which the various insoluble lime salts are thrown down, enable us to subdivide the group of precipitable acids, and even to detect certain individual acids.

§ 64.

6. SULPHATE OF MAGNESIA (Mg O, S O_3, crystallized Mg O, S O_3, H O+6 aq.).

Preparation.—Dissolve 1 part of sulphate of magnesia of commerce in 10 parts of water; if the salt is not perfectly pure, subject it to recrystallization.

Tests.—The solution of sulphate of magnesia must have a neutral reaction. When mixed with sufficient chloride of ammonium it must remain unaffected by ammonia, carbonate and oxalate of ammonia, and sulphide of ammonium for the space of half an hour.

Uses.—Sulphate of magnesia serves almost exclusively for the detection of phosphoric and arsenic acids, which it precipitates from aqueous solutions of their salts in presence of ammonia and

chloride of ammonium, in the form of double salts (basic phosphate or arsenate of magnesia and ammonia), which are nearly insoluble, and have highly characteristic properties. Sulphate of magnesia is, moreover, employed to test the purity of sulphide of ammonium (see § 41).

c. SALTS OF THE OXIDES OF THE HEAVY METALS.

§ 65.

1. Sulphate of Protoxide of Iron (Fe O, S O_3, crystallized Fe O, S O_3, H O+6 aq.).

Preparation.—Heat an excess of iron nails free from rust, or of clean iron wire, with dilute sulphuric acid, until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals with water very slightly acidulated with sulphuric acid, dry, and keep for use. The sulphate of protoxide of iron may also be prepared from the solution of sulphide of iron in dilute sulphuric acid, which is obtained in the process of evolving hydrosulphuric acid.

Tests.—Sulphate of protoxide of iron must appear as fine, pale, green crystals. Those which by action of the air have become yellow, or which give with water a brownish-yellow solution, are to be rejected. The solution, after addition of a little hydrochloric acid, must not be precipitated black by hydrosulphuric acid.

Uses.—Sulphate of protoxide of iron has a great disposition to absorb oxygen, and to be converted into the sulphate of the sesquioxide. It acts, therefore, as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which it separates nitric oxide by withdrawing three atoms of oxygen from it. The decomposition of the nitric acid being attended, in this case, with the formation of a very peculiar brownish-black compound of nitric oxide with an undecomposed portion of the salt of the protoxide of iron, this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Sulphate of protoxide of iron serves, also, for the detection of hydroferricyanic acid, with which it produces a kind of Prussian blue, and also to effect the precipitation of metallic gold from solutions of the salts of that metal.

§ 66.

2. Sesquichloride of Iron (Fe_2 Cl).

Preparation.—Heat in a flask a mixture of 10 parts of water and 1 part of pure hydrochloric acid with small iron nails until no further evolution of hydrogen is observed, even after adding the nails in excess; filter the solution into another flask, and conduct

into it chlorine gas, with frequent shaking, until the fluid no longer produces a blue precipitate in solution of ferricyanide of potassium. Heat until the excess of chlorine is expelled. Dilute until the fluid is twenty times the weight of the iron dissolved, and keep the dilute fluid for use.

Tests.—Solution of sesquichloride of iron must not contain an excess of acid; this may be readily ascertained by stirring a sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate, which shaking the vessel and agitating the fluid fail to redissolve. Ferricyanide of potassium must not impart a blue color to it.

Uses.—Sesquichloride of iron serves to subdivide the group of organic acids which chloride of calcium fails to precipitate; as it produces precipitates in solutions of benzoates and succinates, but not in solutions of acetates and formates. The aqueous solutions of the neutral acetate and formate of sesquioxide of iron exhibit an intensely red color; sesquichloride of iron is, therefore, a useful agent for detecting acetic acid and formic acid. Sesquichloride of iron is exceedingly well adapted to effect the decomposition of phosphates of the alkaline earths (see § 145). It serves also for the detection of hydroferrocyanic acid, with which it produces Prussian blue.

§ 67.

3. Nitrate of Silver ($Ag\,O, N\,O_5$).

Preparation.—Dissolve pure silver* in pure nitric acid, evaporate the solution to dryness, and dissolve 1 part of the salt in 20 parts of water.

Tests.—Solution of nitrate of silver must be completely precipitated by dilute hydrochloric acid, so that the fluid filtered from the precipitated chloride of silver leaves no residue when evaporated on a watch-glass, and is neither precipitated nor colored by hydrosulphuric acid.

[* Obtained from the silver-refiners usually in a state of sufficient purity, or prepared free from all foreign matters by the following method:

Silver coins are dissolved in nitric acid, and the solution is made perfectly clear by rest and decantation, or by filtration. The clear solution is precipitated by excess of common hydrochloric acid, which must also be free from suspended matters, and the precipitated chloride of silver is boiled several times with renewed portions of dilute hydrochloric acid. It is then washed by decantation with hot water until the washings have no longer an acid reaction. The pure chloride of silver thus obtained is mixed, while still moist, with its own weight of crystallized carbonate of soda which has been purified by recrystallization, and ¼ its weight of pure nitre. The mixture is dried, being well stirred during the process, brought into a covered porcelain crucible, heated at first gently, and finally to the fusing point of silver. When cold the globule of silver is removed by breaking the crucible. It is cleaned from adhering flux by thoroughly washing in hot-water.—Mulder.]

Uses.—Oxide of silver forms with many acids soluble, with others insoluble compounds. Nitrate of silver may therefore serve, like chloride of barium, to effect the separation and arrangement of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid; chloride, bromide, iodide, cyanide, ferrocyanide, ferricyanide and sulphide of silver, are insoluble in that menstruum. Nitrate of silver is therefore a most excellent agent to distinguish and separate from all other acids, the hydracids corresponding to the last enumerated compounds of silver. Many of the insoluble salts of silver exhibit a peculiar color (chromate of silver, arsenate of silver), or manifest a characteristic deportment with other reagents, or upon the application of heat (formate of silver); nitrate of silver is therefore an important agent for the positive detection of certain acids.

§ 68.

4. ACETATE OF LEAD (Pb O, $\overline{A}$, crystallized Pb O, $\overline{A}$+3 aq.).

The best acetate of lead of commerce is sufficiently pure for the purpose of chemical analysis; for use, dissolve 1 part of the salt in 10 parts of water.

Tests.—Acetate of lead must dissolve in water to which a few drops of acetic acid have been added, forming a clear and colorless liquid. Hydrosulphuric acid must precipitate all the fixed matter from its solution. Mixed with excess of carbonate of ammonia and filtered, the filtrate must not have a blue color (*copper*).

Uses.—Oxide of lead forms with a great many acids compounds insoluble in water, which are marked either by peculiarity of color or characteristic deportment. The acetate of lead, therefore, produces precipitates in the solutions of these acids, or of their salts, and essentially contributes to the detection of several of them. Thus, chromate of lead, for instance, is characterized by its yellow color, phosphate of lead by its peculiar deportment before the blowpipe, and malate of lead by its ready fusibility.

§ 69.

5. NITRATE OF SUBOXIDE OF MERCURY (Hg_2 O, N O_5, crystallized Hg_2 O, N O_5+2 aq.).

Preparation.—Pour 1 part of pure nitric acid sp. gr. 1.2 on 1 part of mercury, in a porcelain dish, and let the vessel stand twenty-four hours in a cool place; separate the crystals formed from the undissolved mercury and the mother-liquor, and dissolve them in water mixed with one-sixteenth part of nitric acid, by

trituration, in a mortar. Filter the solution, and keep the filtrate in a bottle, with metallic mercury covering the bottom of the vessel.

Tests.—The solution of subnitrate of mercury must yield with dilute hydrochloric acid, a heavy white precipitate of subchloride of mercury. The liquid filtered from this precipitate should give with hydrosulphuric acid none, or only a very slight black precipitate (*sulphide of mercury*).

Uses.—Nitrate of suboxide of mercury acts in an analogous manner to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and, in the second place, it serves for the detection of several readily oxidizable bodies, *e. g.*, of formic acid, as the oxidation of such bodies, at the expense of the oxygen of the suboxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 70.

6. Chloride of Mercury (Hg Cl).

The chloride of mercury of commerce is sufficiently pure for the purpose of chemical analysis. For use, dissolve 1 part of the salt in 16 parts of water.

Uses.—Chloride of mercury gives with several acids, *e. g.*, with hydriodic acid, peculiarly colored precipitates, and may accordingly be used for the detection of these acids. It is an important agent for the detection of tin, when that metal is in solution in the state of protochloride; if only the smallest quantity of that compound is present, the addition of chloride of mercury in excess to the solution is followed by separation of subchloride of mercury insoluble in water. In a similar manner chloride of mercury serves also for the detection of formic acid.

§ 71.

7. Sulphate of Copper (Cu O, S O_3, crystallized Cu O, S O_3, H O + 4 aq.).

Preparation.—This reagent may be obtained in a state of great purity from the residue remaining in the retort in the process of preparing bisulphite of soda (§ 49), by treating that residue with water, applying heat, filtering, crystallizing, and purifying the salt by recrystallization. For use, dissolve 1 part of the pure crystals in 10 parts of water.

Tests.—Pure sulphate of copper must be completely precipitated from its solutions by hydrosulphuric acid; ammonia and sulphide of ammonium must accordingly leave the filtrate unaltered.

Uses.—Sulphate of copper is employed in qualitative analysis to

effect the precipitation of hydriodic acid in the form of subiodide of copper. For this purpose it is necessary to mix the solution of 1 part of sulphate of copper with 2½ parts of sulphate of protoxide of iron, otherwise half of the iodine will separate in the free state. The protoxide of iron changes, in this process, to sesquioxide, at the expense of the oxygen of the oxide of copper, which latter is thus reduced to the state of suboxide. Sulphate of copper is used also for the detection of arsenious and arsenic acid; it serves, likewise, as a test for the soluble ferrocyanides.

§ 72.

8. PROTOCHLORIDE OF TIN (Sn Cl, crystallized Sn Cl+2 aq.).

Preparation.—Reduce English tin to powder by means of a file, or fuse it in a small porcelain dish, remove from the fire, and triturate the fused liquid mass with a pestle until it has passed again to the solid state; boil the powder for some time with concentrated hydrochloric acid in a flask (taking care always to have an excess of tin) until no more hydrogen gas is evolved; dilute the solution with 4 times the quantity of water slightly acidulated with hydrochloric acid, and filter. Keep the filtrate for use in a well-stoppered bottle containing small pieces of metallic tin, or some pure tin-foil. If these precautions are neglected, the protochloride will soon change to bichloride with separation of oxychloride, which will, of course, render the reagent totally unfit for the purpose for which it is intended.

Tests.—Solution of protochloride of tin, when added to a solution of chloride of mercury, must immediately produce a white precipitate of subchloride of mercury; when treated with hydrosulphuric acid, it must give a dark brown precipitate; it must not be precipitated nor rendered turbid by sulphuric acid.

Uses.—The great tendency of protochloride of tin to absorb oxygen, and thus to form binoxide, or rather bichloride—as the binoxide, in the moment of its formation, decomposes with the free hydrochloric acid present—makes this substance one of our most powerful reducing agents. We employ it in the course of analysis as a test for mercury, and also to effect the detection of gold, for which latter purpose it is previously mixed with some nitric acid, without heat.

§ 73.

9. BICHLORIDE OF PLATINUM (Pt Cl_2, crystallized Pt Cl_2 + 10 aq.).

Preparation.—Treat platinum filings (purified by boiling with nitric acid), with concentrated hydrochloric acid and some nitric acid, in a narrow-necked flask, and apply a very gentle heat, adding occasionally fresh portions of nitric acid, until the platinum is

completely dissolved.* Evaporate the solution to dryness on the water-bath, with addition of hydrochloric acid, and dissolve the residue in 10 parts of water for use.

Tests.—Bichloride of platinum must, upon evaporation to dryness in the water-bath, leave a residue which dissolves completely in spirit of wine.

Uses.—Bichloride of platinum forms very sparingly soluble double salts with chloride of potassium and chloride of ammonium, but not so with chloride of sodium; it serves, therefore, to detect ammonia and potassa, and is, indeed, almost our most delicate reagent for the latter substance.

§ 74.

10. SODIO-PROTOCHLORIDE OF PALLADIUM (Na Cl, Pd Cl).

Dissolve 5 parts of palladium in nitrohydrochloric acid (comp. § 73), add 6 parts of pure chloride of sodium, evaporate in the water-bath to dryness, and dissolve 1 part of the residuary double salt in 12 parts of water for use. The brownish solution forms an excellent means of detecting and separating iodine.

§ 75.

11. TERCHLORIDE OF GOLD (Au Cl_3).

Preparation.—Take fine shreds of gold, which may be alloyed with silver or copper, treat them in a flask with nitrohydrochloric acid in excess, and apply a gentle heat until no more of the metal dissolves. If the gold was alloyed with copper, which is known by the brownish-red precipitate produced by ferrocyanide of potassium in a portion of the solution diluted with water, mix it with solution of sulphate of protoxide of iron in excess; this will reduce the terchloride to metallic gold, which will separate in the form of a fine brownish-black powder; wash the powder in a small flask, and redissolve it in nitrohydrochloric acid; evaporate the solution to dryness on the water-bath, and dissolve the residue in 30 parts of water. If the gold was alloyed with silver, the latter metal remains as chloride upon treating the alloy with nitrohydrochloric acid. In that case evaporate the solution at once to dryness, and dissolve in water for use.

[* When platinum scraps are to be converted into bichloride, the process of solution is extremely tedious, unless the metal be first brought to a state of fine division. This is most conveniently effected as follows: Heat in a clay crucible 5 parts of zinc to fusion, with sufficient common salt to cover the surface and prevent its oxidation, then introduce 1 part of platinum scraps in small quantities at a time, into the fused metal. An alloy is formed from which the zinc is to be removed by digesting in common somewhat dilute hydrochloric acid, until all effervescence ceases, and subsequent boiling for a time with fresh hydrochloric acid. The residual platinum is completely washed with water and boiled with nitric acid. It is again washed, and finally treated with aqua regia, as above directed.]

Uses.—Terchloride of gold has a great tendency to yield up its chlorine; it therefore readily converts protochlorides into higher chlorides, protoxides, with the co-operation of water, into higher oxides. These peroxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis this reagent is used only for the detection of protoxide of tin, in the solutions of which it produces a purple color or a purple precipitate.

V. COLORING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

§ 76.

1. Test Papers.

α. Blue Litmus Paper.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the one part, by repeatedly stirring with a glass rod dipped in very dilute sulphuric acid, until the color of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of fine unsized paper through it; suspend these slips over threads and leave them to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark.

Uses.—Litmus paper serves to detect the presence of free acid in fluids, as acids change its blue color to red. It must be borne in mind, however, that the soluble neutral salts of most of the heavy metallic oxides produce the same effect.

β. Reddened Litmus Paper.

Preparation.—Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Steep slips of paper in the solution, and dry them as in α. The dried slips must look distinctly red.

Uses.—Pure alkalies and alkaline earths, and also the sulphides of their metals, restore the blue color of reddened litmus paper; alkaline carbonates and the soluble salts of several other weak acids, especially of boracic acid, possess the same property. This reagent serves therefore for the detection of these bodies in general.

γ. Georgina Paper (*dahlia paper*).

Preparation.—Boil the violet-colored petals of *Georgina purpurea* (purple dahlia) in water, or digest them with spirit of wine, and steep slips of paper in the tincture obtained. The latter should

be neither more nor less concentrated than is necessary to make the paper, after drying, appear of a fine and light violet blue color. Should the color too much incline to red, this may be remedied by adding a very little ammonia to the tincture.

Uses.—Georgina paper is reddened by acids, whilst alkalies impart a beautiful green tint to it. It is therefore an extremely convenient substitute both for the blue and the reddened litmus paper. This reagent, if properly prepared, is a most delicate test both for acids and alkalies. Concentrated solutions of caustic alkalies turn Georgina paper yellow, by destroying the coloring matter.

δ. Turmeric Paper.

Preparation.—Digest and heat 1 part of bruised turmeric root with six parts of weak spirit of wine, filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

Uses.—Turmeric paper serves, like reddened litmus paper and dahlia paper, for the detection of free alkalies, &c., as they change its yellow color to brown. It is not quite so delicate a test as the other reagent papers; but the change of color which it produces is highly characteristic, and is very distinctly perceptible in many *colored* fluids; we cannot well dispense, therefore, with this paper. When testing with turmeric paper, it is to be borne in mind that, besides the substances enumerated in β, several other bodies (boracic acid, for instance) possess the property of turning its yellow color to brown-red. It affords an excellent means for the detection of the latter substance.

All test papers are cut into slips, which are kept in small well-closed boxes, or in bottles covered with black paper, as continued action of light destroys the color.

§ 77.

2. Solution of Indigo.

Preparation.—Take from 4 to 6 parts of fuming sulphuric acid, add slowly, and in small portions at a time, 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns deep blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo is thereby destroyed; it is therefore advisable, when dissolving larger quantities of the substance, to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into 20 times the quantity of water, mix, filter, and keep the filtrate for use.

Uses.—Indigo is decomposed by boiling with nitric acid, yellow-colored oxidation products being formed. It serves, therefore, for the detection of nitric acid. Solution of indigo is also well adapted to effect the detection of chloric acid and of free chlorine.

B. REAGENTS IN THE DRY WAY.

I. Fluxes and Decomposing Agents.

§ 78.

1. Mixture of Carbonate of Soda and Carbonate of Potassa ($Na\ O, C\ O_2 + K\ O, C\ O_2$).

Preparation.—Digest 10 parts of purified bitartrate of potassa in powder with 10 parts of water and 1 part of hydrochloric acid for several hours on the water-bath, with frequent stirring; put the mass into a funnel with a small filter inserted into the pointed end; let it drain; cover with a disc of rather difficultly permeable filtering paper with upturned edges, and wash by repeatedly pouring upon this small quantities of cold water; continue this washing process until the fluid running off is no longer rendered turbid by solution of nitrate of silver, after addition of nitric acid. Dry the bitartrate of potassa freed in this manner from lime (and phosphoric acid). It is now necessary to prepare pure nitrate of potassa. To effect this, dissolve nitrate of potassa of commerce in half its weight of boiling water, filter the solution into a porcelain or stoneware dish, using a hot funnel, and stir it well with a wooden or porcelain spatula until cold. Transfer the crystalline powder to a funnel loosely stopped with cotton, let it drain, press down tight, make it even at the top, and cover with a double disc of difficultly permeable filtering paper with upturned edges, and pour upon this at proper intervals small portions of water, until the washings are no longer made turbid by solution of nitrate of silver. Empty now the contents of the funnel into a porcelain dish, dry in this vessel, and reduce the mass to a fine powder by trituration. Mix now 2 parts of the pure bitartrate of potassa with 1 part of the pure nitrate of potassa; put the perfectly dry mixture in small portions at a time into a clean-scoured cast-iron pot heated to gentle redness; when the mixture has deflagrated, heat strongly, until a sample taken from the edges gives with water a perfectly colorless solution. Triturate the charred mass with water, filter, wash slightly, and evaporate the filtrate in a porcelain, or, better still, in a silver dish, until the fluid is covered with a persistent pellicle. Let the mixture now cool, with constant stirring; put the crystals of carbonate of potassa on a funnel, let them well drain, wash slightly, dry thoroughly in a silver or porcelain dish, and keep the crystals in a well-stoppered bottle. The mother-liquor leaves, upon evaporation,

a salt which, though containing traces of alumina and silicic acid, may still be turned to account for many purposes.

Mix 13 parts of the pure carbonate of potassa prepared in the manner just now described, with 10 parts of pure anhydrous carbonate of soda, and keep the mixture in a well-stoppered bottle. The mixture of carbonate of potassa and carbonate of soda may also be prepared by deflagrating 20 parts of pure bitartrate of potassa with 9 parts of pure nitrate of soda, treating with water, and evaporating the solution to dryness.

Tests.—The purity of the mixed salt is tested as directed, § 47 (*carbonate of soda*). Should cyanide of potassium be present, it is detected by adding a mixture of protosulphate and sesquichloride of iron, and then hydrochloric acid in excess. A bluish green color is produced and a blue precipitate separates after long standing.

Uses.—If silicic acid or silicates are fused with about 4 parts (consequently with an excess) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate, hydrochloric acid separates the silicic acid as hydrate. If a fixed alkaline carbonate is fused together with sulphate of baryta, strontia, or lime, there are formed carbonates of the alkaline earths and sulphate of the alkali, in which new compounds both the base and the acid of the originally insoluble salt may now be readily detected. However, we do not employ carbonate of potassa separately, nor carbonate of soda, to effect the decomposition of the insoluble silicates and sulphates; but we apply for this purpose the above-described mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its two components, and thus enables us to conduct the operation over a *Berzelius* lamp, or over a simple gas-lamp. [It is far better to be provided with a blast lamp (*Bunsen's*) or a wind-furnace and employ *carbonate of soda alone* for fluxing silicates, &c., than to take the trouble to prepare pure carbonate of potassa for this mixture.] The fusion with alkaline carbonates is invariably effected in a platinum crucible, provided no reducible metallic oxides be present.

§ 79.

2. Hydrate of Baryta (Ba O, H O).

Preparation.—The crystals of baryta prepared in the manner directed, § 34, are heated gently in a silver or platinum dish, until the water of *crystallization* is completely expelled. The residuary white mass is pulverized, and kept for use in a well-closed bottle.

Uses.—Hydrate of baryta fuses at a gentle red heat without losing its water. Upon fusing silicates together with about 4 parts of hydrate of baryta, a basic silicate of baryta is formed, and the oxides are liberated. If the fused mass is treated with hydrochloric acid, the solution evaporated to dryness, and the residue digested with hydrochloric acid, the silicic acid is left behind, and the oxides are obtained in solution in the form of chlorides. We use hydrate of baryta as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to the carbonate or nitrate of baryta, since it does not require a very high temperature for its fusion, as is the case with the carbonate, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the nitrate. The operation is conducted in silver or platinum crucibles.

§ 80.

3. Fluoride of Calcium (Ca Fl).

Take fluor-spar as pure as can be procured, and more particularly free from alkalies, reduce to fine powder, and keep this for use.

Uses.—Fluoride of calcium applied in conjunction with sulphuric acid, serves to effect the decomposition of silicates insoluble in acids, and more especially to detect the alkalies which they contain. Compare Section III. *Silicic acid*, § 153.

[§ 81.

4. Carbonate of Lime (Ca O C O_2).

Preparation.—Solution of pure chloride of calcium, § 63, is heated to boiling and precipitate by a slight excess of solution of carbonate of ammonia with addition of some ammonia, § 48. The precipitate is washed 5 or 6 times with hot water by decantation, then is brought upon a filter and further edulcorated until the washings give no turbidity with nitrate of silver. The contents of the filter are then dried and bottled.

Tests.—Carbonate of lime for use as a flux, must be free from salts of the fixed alkalies. When washed with hot water the washings must yield no residue when evaporated to dryness. For uses, see chloride of ammonium, § 82.]

[§ 82.

5. Chloride of Ammonium (N H_4 Cl).

Preparation.—Crystals of chloride of ammonium, prepared as described in § 54, are dried and preserved in a wide-mouthed bottle.

Tests.—The salt must be free from salts of the fixed alkalies.

A considerable quantity of the salt, when ignited in a platinum vessel, must leave no residue.

Uses.—When a silicate containing alkalies, that is insoluble in acids, is intimately mixed in a state of fine powder with chloride of ammonium and carbonate of lime, in suitable proportions, and heated for some time in a platinum crucible, a mass results, from which hot water extracts, besides caustic lime and chloride of calcium, the alkalies of the silicate in the form of chlorides; while the silica and other bases remain behind undissolved. Carbonate (or oxalate) of ammonia may be used to remove the lime from the solution, and the filtrate on evaporation to dryness, and ignition yields the alkalies as pure chlorides (or carbonates). In this operation the larger share of the carbonate of lime, at a red heat, loses carbonic acid and is converted into caustic lime. A smaller portion, by the action of chloride of ammonium, is converted into chloride of calcium, which, readily fusing, allows the lime and silicate to come into intimate contact, whereby insoluble basic silicate of lime and soluble alkaline chlorides result.—(*J. Lawrence Smith.*) This is incomparably the best method of fluxing silicates for the separation of the alkalies. See § 210. 2. *c.*]

§ 83.

6. Nitrate of Soda (NaO, NO_5).

Preparation.—Neutralize pure nitric acid with pure carbonate of soda exactly, and evaporate to crystallization. Dry the crystals thoroughly, triturate, and keep the powder for use.

Tests.—A solution of nitrate of soda must not be made turbid by solution of nitrate of silver or nitrate of baryta, nor precipitated by carbonate of soda.

Uses.—Nitrate of soda serves as a very powerful oxidizing agent, by yielding oxygen to combustible substances when heated with them. We use this reagent principally to convert several metallic sulphides, and more particularly the sulphides of tin, antimony, and arsenic, into oxides and acids; and also to effect the rapid and complete combustion of organic substances; for the latter purpose, however, nitrate of ammonia is in many cases preferable; this latter reagent is prepared by saturating nitric acid with carbonate of ammonia.

II. Blowpipe Reagents.

§ 84.

1. Carbonate of Soda (NaO, CO_2).

Preparation.—See § 47.

Uses.—Carbonate of soda serves, in the first place, to promote the reduction of oxidized substances in the inner flame of the blow-

pipe. In fusing it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. It co-operates in this process also chemically by the transposition of its constituents (according to *R. Wagner*, in consequence of the formation of cyanide of sodium). If the quantity operated upon was very minute, the reduced metal is often found in the pores of the charcoal. In such cases, the parts surrounding the little cavity which contained the sample are dug out with a knife, and triturated in a small mortar; the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small flat spangles, according to the nature of the particular metal or metals present.

Carbonate of soda serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in fusing carbonate of soda. A few only of the bases dissolve in fusing carbonate of soda, but acids dissolve in it with facility. Carbonate of soda is, moreover, applied as a decomposing agent and flux, and more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly formed sulphate of soda being reduced at the same time to sulphide of sodium; and to effect the decomposition of sulphide of arsenic, with which it forms a double sulphide of arsenic and sodium, and arsenite or arsenate of soda, thus converting it to a state which permits its subsequent reduction by hydrogen. Finally, carbonate of soda is the most sensitive reagent in the dry way for the detection of manganese, since when fused in the outer flame of the blowpipe together with a substance containing manganese, it produces a green opaque bead, owing to the formation of manganate of soda.

§ 85.

2. Cyanide of Potassium (K Cy).

Preparation.—See § 55.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from sulphur compounds: this reduction is attended in the former case with formation of cyanate of potassa, by the absorption of oxygen, and in the latter case with formation of sulphocyanide of potassium. By means of this reagent we may effect the reduction of metals from their compounds with the greatest possible facility; thus we may, for instance, produce metallic antimony from antimonious acid or from sulphide of antimony, metallic iron from sesquioxide of iron, &c.

The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit-lamp. Cyanide of potassium is a most valuable and important agent to effect the reduction of arsenites and arsenates, and more particularly of tersulphide of arsenic (see § 135). Cyanide of potassium is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like binoxide of tin, bisulphide of tin, &c., the reduction of which by means of carbonate of soda requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blowpipe experiments we invariably use a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended here to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has, moreover, this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 86.

3. BIBORATE OF SODA (*Borax*) ($Na\ O, 2\ B\ O_3$, crystallized + 10 aq.).

The purity of commercial borax may be tested by adding to its solution carbonate of soda, or after previous addition of nitric acid, solution of nitrate of baryta or of nitrate of silver. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure crystallized borax is pulverized and kept for use.

Uses.—Boracic acid manifests a great affinity for oxides when brought into contact with them in a state of fusion. This affinity enables it in the first place, to combine directly with oxides; secondly, to expel weaker acids from their salts; and, thirdly, to dispose metals, sulphides, and haloid compounds to oxidize in the outer flame of the blowpipe, that it may combine with the oxides. Most of the thus produced borates fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or by the formation of double salts. Now, in the biborate of soda we have both free boracic acid and borate of soda; the union of these two substances renders it one of our most important blowpipe reagents. In the process of fluxing with borax, we usually select platinum wire for a support; the loop of the wire is heated to red-

ness, then dipped into the powder, and exposed to the outer flame; a colorless bead of fused borax is thus produced. A small portion of the substance under examination is then attached to the bead, by bringing the latter into contact with it, either whilst still hot or having previously moistened it. The bead with the sample of the substance intended for analysis adhering to it, is now exposed to the blowpipe flame, and the phenomena to the manifestation of which this process gives rise are carefully observed and examined. The following points ought to be more particularly watched:—(1) Whether or not the sample under examination dissolves to a transparent bead, and whether or not the bead retains its transparency on cooling; (2) whether the bead exhibits a distinct color, which in many cases at once clearly indicates the individual metal which the analysed compound contains, as is the case, for instance, with cobalt; and (3) whether the bead manifests the same or a different deportment in the outer and in the inner flame. Phenomena of the latter kind arise from the ensuing reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 87

4. PHOSPHATE OF SODA AND AMMONIA (*Microcosmic Salt or Salt of Phosphorus*) ($Na\,O, N\,H_4\,O, H\,O, P\,O_5$, crystallized + 8 aq.).

Preparation.—*a.* Heat to boiling 6 parts of phosphate of soda and 1 part of pure chloride of ammonium with 2 parts of water, and let the solution cool. Free the crystals produced of the double phosphate of soda and ammonia by recrystallization from the chloride of sodium which adheres to them. Dry the purified crystals, and pulverize them for use.

b. Of two equal parts of common pure phosphoric acid, 1 part has soda-lye and the other ammonia added until both liquids acquire a decided alkaline reaction. They are then mixed together and evaporated to crystallization.

Tests.—Phosphate of soda and ammonia should dissolve in water to a solution having a slightly alkaline reaction. The yellow precipitate produced in it by nitrate of silver must perfectly dissolve in nitric acid. Fused on platinum wire it must give a clear and colorless bead.

Uses.—When phosphate of soda and ammonia is subjected to the action of heat, the ammonia escapes with the water of crystallization, and readily fusible metaphosphate of soda is left behind. The action of microcosmic salt is quite analogous to that of biborate of soda. We prefer it, however, in some cases, to borax as a solvent or flux, the beads which it forms with many substances being

more beautifully and distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop of the wire must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed in the preceding paragraph.

§ 88.

5. NITRATE OF PROTOXIDE OF COBALT (Co O, N O_5, crystallized + 5 aq.).

Preparation.—Fuse in a Hessian crucible 3 parts of bisulphate of potassa, and add to the fused mass, in small portions at a time, 1 part of well roasted cobalt ore (the purest zaffre you can procure) reduced to fine powder. The mass thickens, and acquires a pasty consistence. Heat now more strongly, until it has become more fluid again, and continue to apply heat until the excess of sulphuric acid is *completely* expelled, and the mass accordingly no longer emits white fumes. Remove the fused mass now from the crucible with an iron spoon or spatula, let it cool, and reduce it to powder; boil this with water until the undissolved portion presents a soft mass; then filter off the rose-red solution, which is free from arsenic and nickel, and mostly also from iron.

Add to this liquid a little carbonate of soda so as to separate a small quantity of carbonate of cobalt, boil and filter. The solution, which is now free from oxide of iron, is precipitated boiling hot with carbonate of soda, the precipitate is thoroughly washed, and treated while still moist with excess of oxalic acid. The rose-red oxalate of cobalt thus procured is washed, dried, and ignited in a glass tube in a stream of hydrogen gas.* It is hereby converted into carbonic acid which escapes and metallic cobalt. The latter is washed, first with water containing some acetic acid, and afterwards with pure water, and then dissolved in dilute nitric acid. The solution, if needful, is treated with hydrosulphuric acid gas to separate copper, and filtered again. It is lastly evaporated to dryness and the residue dissolved in 10 times its weight of water.

Tests.—Solution of nitrate of protoxide of cobalt must be free from other metals, and especially also from salts of the alkalies; when precipitated with sulphide of ammonium and filtered, the filtrate must, upon evaporation on platinum, leave no fixed residue.

Uses.—Protoxide of cobalt forms, upon ignition with certain infusible bodies, peculiarly colored compounds, and may accordingly serve for the detection of these bodies (oxides of zinc, alumina, and magnesia; see Section III.).

[* Most conveniently supplied from one of the forms of gas-generating apparatus described in § 30.]

SECTION III.

ON THE DEPORTMENT OF BODIES WITH REAGENTS.

§ 89.

I STATED in my introductory remarks that the operations and experiments of qualitative analysis have for their object the conversion of the *unknown* constituents of any given compound into forms of which we *know* the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the several constituents of which the analysed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, no matter whether of a positive or negative nature. But as a question does not render us any the wiser if we do not know the language in which the answer is returned, so, in like manner, will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of our reagents upon the substance examined.

Before we can therefore proceed to enter upon the practical investigations of analytical chemistry, it is indispensable that we should *really* possess the most perfect knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances we wish to analyse. Now, this perfect knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds and the manifestation of the various reactions; and, in the second place, in a distinct impression of the color, form, and physical properties which characterize the new compound. This section of the work demands therefore not only the most careful and attentive study, but requires moreover that the student should *examine and verify by actual experiment every fact asserted in it.*

The method usually adopted in elementary works on chemistry is to treat of the various substances and their deportment with reagents individually and separately, and to point out their characteristic reactions. I have, however, in the present work, deemed it more judicious and better adapted to its elementary character, to arrange those substances which are in many respects analogous into groups, and thus, by comparing their analogies with their differences, to place the latter in the clearest possible light.

A.—Deportment and Properties of the Metallic Oxides and of their Radicals.

§ 90.

Before proceeding to the special study of the several metallic oxides, I give here a general view of the whole of them, classified in groups—showing *which* oxides belong to each group. The *grounds* upon which the classification has been arranged will appear from the special consideration of the several groups.

First group—

Potassa, soda, ammonia (caesia, rubidia, lithia).

Second group—

Baryta, strontia, lime, magnesia.

Third group—

Alumina, sesquioxide of chromium (glucina, thoria, yttria, terbia, erbia, zirconia; oxides of cerium, lanthanum, didymium; oxide of titanium and titanic acid; tantalic acid, hyponiobic acid).

Fourth group—

Oxides of *zinc, manganese, nickel, cobalt, iron* (uranium, vanadium, thallium).

Fifth group—

Oxides of *silver, mercury, lead, bismuth, copper, cadmium* (palladium, rhodium, osmium, ruthenium).

Sixth group—

Oxides and acids of *gold, platinum, tin, antimony, arsenic* (iridium, molybdenum, tellurium, tungsten, selenium).

Of these metallic oxides only those printed in *italics* are found extensively and in large quantities in that portion of the earth's crust which is accessible to our investigations; these, therefore, are most important to chemistry, arts and manufactures, agriculture, pharmacy, &c. &c.; and these therefore we shall dwell upon at greater length. The remainder are more briefly considered in supplementary paragraphs, which are printed in smaller type, so that they can be omitted by the beginner without inconvenience.

The deportment of the metals I have given only in the case of those that are more frequently met with, in analytical operations, in the metallic state.

§ 91.

First group. Alkalies.

Of common occurrence: Potassa, Soda, Ammonia.

Of rare occurrence: Caesia, Rubidia, Lithia.

Properties of the group.—The alkalies are readily soluble in water, as well in the pure or caustic state as in the form of sulphides, carbonates, and phosphates. Accordingly they do not precipitate

one another in the pure state, nor as carbonates or phosphates, nor are they precipitated by hydrosulphuric acid under any condition whatever. The solutions of the pure alkalies, as well as of their sulphides and carbonates, restore the blue color of reddened litmus-paper, and impart an intensely brown tint to turmeric paper.

Special Reactions of the more common Alkalies.

§ 92.

a. POTASSA (K O).

1. POTASSA and its HYDRATE and SALTS are not volatile at a faint red-heat. Potassa and its hydrate deliquesce in the air; the oily liquids formed do not solidify by absorption of carbonic acid.

2. Nearly the whole of the SALTS OF POTASSA are readily soluble in water. They are colorless, if the constituent acid is so. The neutral (see § 21) salts of potassa with strong acids do not alter vegetable colors. Carbonate of potassa crystallizes with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous, and suffers no alteration in the air.

3. *Bichloride of platinum* produces in the neutral and acid solutions* of the salts of potassa a yellow, crystalline, heavy precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (*platinchloride of potassium*) (K Cl, Pt Cl_2). In concentrated solutions this precipitate separates immediately upon the addition of the reagent: in dilute solutions it forms only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernable under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the bichloride of platinum is added. The precipitate is difficultly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Bichloride of platinum is therefore a particularly delicate test for salts of potassa dissolved in spirit of wine. The best method of applying this reagent is to evaporate the aqueous solution of the potassa salt with bichloride of platinum nearly to dryness on the water-bath, and to pour a little water on the residue, or, better still, some spirit of wine, provided no substances insoluble in that menstruum be present: the platinchloride of potassium

* [While a *neutral salt* is one whose acid and base bear a certain ratio to each other—an *acid salt* being one that contains a larger proportion of acid, and a *basic salt* one in which a larger proportion of *base* (alkali or other metallic oxide) exists; a *neutral solution* is simply one which is indifferent to vegetable colors—litmus, turmeric. (§ 76.) or has a *neutral reaction*; an *acid solution* is one which has an *acid reaction*—reddens blue litmus; an *alkaline solution* is one that *reacts alkaline*—tinges turmeric paper brown.]

is left undissolved. Care must be taken not to confound this double salt with platinchloride of ammonium, which greatly resembles it (see § 94.4).

4. *Tartaric acid* produces in neutral or alkaline solutions of salts of potassa—(in the latter case tartaric acid must be added to strong acid reaction)—a white, quickly subsiding, *granular* crystalline precipitate of BITARTRATE OF POTASSA ($K\,O, H\,O, C_8\,H_4\,O_{10}$). In concentrated solutions this precipitate separates immediately; in dilute solutions often only after the lapse of some time. Vigorous shaking or stirring of the fluid promotes its formation considerably. Very dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but pretty readily soluble in hot water. In the case of acid solutions, the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda, before we can proceed to test for potassa with tartaric acid.

Bitartrate of Soda (§ 25) is even a better test of potassa than tartaric acid. It precipitates bitartrate of potassa like tartaric acid, but is a more sensitive reagent than the latter, because its soda neutralizes the acid of the potassa salt under examination, and thus prevents any solvent action of this acid on the bitartrate of potassa. (*e. g.* $K\,O, N\,O_5 + Na\,O, H\,O, C_8\,H_4\,O_{10} = K\,O, H\,O, C_8\,H_4\,O_{10} + Na\,O, N\,O_5$).

5. If any salt of potassa that is volatile at a bright red heat, be brought by means of a platinum wire into the *zone of fusion* of the Bunsen gas-lamp (§ 14), or into the *inner blowpipe flame*,* it is vaporized and communicates to the flame a BLUISH-VIOLET color. Chloride of potassium and nitrate of potassa volatilize rapidly, carbonate and sulphate of potassa more slowly, phosphate of potassa still more slowly; all, however, give the reaction with distinctness. If it is desired to render the coloration of the flame independent of any acid which is accidentally present, and which may impede the reaction, the substance under examination is moistened with sulphuric acid and dried at the edge of the flame before the reaction is observed; or, in case of silicates and other very fixed compounds, the substance is fused with pure gypsum. There is thus formed sulphate of potassa (in the latter instance silicate of lime also) which cannot fail to tinge the flame violet, *unless soda is present*, when the reaction is more or less masked according to the quantity of the latter, only a small proportion of it being requisite to obscure the potassa flame entirely.

6. The *spectrum* of the potassa flame as seen in the *spectroscope*

* Salts which decrepitate are ignited in a platinum spoon before one attempts to fix them on the wire.

(§ 15), is mapped on Plate 1. It contains two lines that are especially characteristic, viz., the red α and the indigo-blue β.

7. When the potassa flame is observed through the *indigo prism* (§ 15), its color appears sky-blue, violet, and through the thickest part of the prism even intense carmine-red. Salts of lime, soda, and lithia in admixture do not affect this reaction, because the yellow soda rays (§ 93, 3) cannot penetrate the indigo-prism at all, and the lithia rays can only pass the thinner parts of the prism*. Organic matters which make the flame luminous may occasion mistakes, and should therefore be destroyed by heat. Instead of the indigo prism, cobalt glass (§ 14) may be employed; it should be so thick, or so many thicknesses should be used, as totally to absorb the red rays of a lithia flame.

8. If a salt of potassa (more particularly chloride of potassium) is heated with a small quantity of water, alcohol (burning with colorless flame) added, heated, and then kindled, the *flame* appears VIOLET. The reaction is far less delicate than that given in 5, and presence of soda obscures it entirely.

§ 93.

b. SODA (Na O).

1. SODA and its HYDRATE and SALTS presents in general the same deportment and properties as potassa and its corresponding compounds. The oily fluid which soda forms by deliquescing in the air, resolidifies speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily; the tabular crystals (Na O, C O_2 + aq.) effloresce rapidly when exposed to the air. The same applies to the prismatic crystals of sulphate of soda (Na O, S O_3 + 10 aq.).

2. If to a sufficiently concentrated neutral or alkaline solution of a soda salt, which is conveniently placed on a watch-glass, solution of *granular antimonate of potassa* (prepared as directed in § 52) is added, there appears at first only a slight turbidity or none at all. On rubbing the bottom of the watch-glass with a glass rod, there speedily separates a crystalline precipitate of ANTIMONATE OF SODA (Na O, Sb O_5 + 7 *aq.*), which at first appears on the track of the glass rod, and settles from the liquid as a heavy sandy deposit. From dilute solutions it is formed only after the lapse of some time, *e. g.*, 12 hours; in very dilute liquids it does not appear at all. The precipitate *always* has a distinct crystalline character. When slowly formed, it sometimes assumes the shape of well defined microscopic square octahedrons, sometimes of four sided prisms with pyramidal terminations; when it separates rapidly it appears in minute boat-shaped crystals. The presence of large quantities of

* The prism should be marked at the point where the lithia rays cease to be perceptible through it.

potassa-salts very perceptibly diminishes the delicacy of the reaction. Acid solutions cannot be tested with antimonate of potassa, because free acid precipitates from this reagent hydrated antimonic acid or acid antimonate of potassa. If, therefore, free acid be present, it must be removed, if possible, by evaporation or ignition, or neutralized by addition of carbonate of potassa, before the reagent is applied. This test is only applicable to such solutions as contain no other bases than potassa and soda.

3. When salts of soda are brought into the *zone of fusion* of the Bunsen lamp, or into the *inner blowpipe flame*, they evince, as to their volatility and deportment towards decomposing agents, a behavior similar to that of salts of potassa. The soda-salts are, however, somewhat less volatile than the corresponding potassa salts. Highly characteristic for soda is the *intense yellow color* it communicates to the flame, a reaction which serves for detecting the minutest traces of soda, and which is not masked by the presence of large quantities of potassa-salts.

4. *The Spectrum* of soda, Plate 1, contains a single yellow line. *α*. The spectral reaction is so extraordinarily sensitive, that, as a rule, the quantity of soda contained in the atmospheric dust suffices to give at least a faint yellow line.

5. The soda-flame is characterized by its rendering a crystal of *bichromate of potassa*, which is illuminated by its light, colorless. Paper covered with *iodide of mercury* when seen by the soda-flame, appears yellowish-white (*Bunsen*). Viewed through *green glass* its color is orange-yellow (*Merz*). These reactions are not disguised by presence of salts of potassa, lithia, or lime.

6. If a salt of soda (more particularly chloride of sodium) is heated with a small quantity of water, *alcohol* added, and the latter heated and then kindled, the flame appears strongly YELLOW. The presence of a salt of potassa does not impair the distinctness of this reaction.

7. *Bichloride of Platinum* gives no precipitate in solutions of salts of soda. The BICHLORIDE OF PLATINUM AND CHLORIDE OF SODIUM (*platinchloride of sodium*) is easily soluble both in water and alcohol. From concentrated solutions it crystallizes in aurora-red prisms. [The form of these crystals is characteristic for soda when no other bases but potassa or ammonia are present. By slowly evaporating a drop of the solution of chloride of sodium to which *excess* of bichloride of platinum has been added, on a slip of glass, the crystals appear as needles or long prisms, usually distinguishable by the naked eye, and readily made out by help of a magnifier.]

8. *Tartaric acid* and *Bitartrate of soda* do not precipitate even concentrated neutral solutions of salts of soda.

§ 94.

c. Ammonia ($N H_4 O$).

1. Anhydrous AMMONIA ($N H$) is gaseous at the common temperature; but we have most frequently to deal with it in its aqueous solution, in which it betrays its presence at once by its penetrating odor. It is expelled from this solution by the application of heat. It may be assumed that the solution contains it as oxide of ammonium ($N H_4 O$) (see § 33).

2. All the SALTS OF AMMONIA are volatile at a high temperature, either with or without decomposition. Most of them are readily soluble in water. The solutions are colorless. The neutral compounds of ammonia with strong acids do not alter vegetable colors.

3. If salts of ammonia are triturated together with *hydrate of lime*, best with the addition of a few drops of water, or are, either in a solid form or in solution, heated with solution of soda or of potassa, the ammonia is liberated in the gaseous state, and betrays itself (1) by its characteristic *odor;* (2) by its *reaction* on moistened test-papers; and (3) by giving rise to the formation of *white fumes*, when any object (*e. g.*, a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes arise from the formation of solid ammoniacal salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, admits less readily of a mistake. In cases where the quantity of ammonia present is only very small, the best way of testing the alkaline reaction of the fumes is to cover a small beaker containing the mixture of the substance with hydrate of lime and a *very little* water, with a watch-glass, having a slip of moistened turmeric or reddened litmus paper attached to the convex side, to place it in hot sand, and observe, after a few minutes, whether the test-paper has changed color.

4. *Bichloride of platinum* shows the same deportment with salts of ammonia as with salts of potassa; the yellow precipitate of BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM (*platinchloride of ammonium* $N H_4 Cl, Pt Cl_2$) is, however, of a somewhat lighter color than platinchloride of potassium. It consists, like the corresponding potassium compound, of octahedrons, discernable under the microscope.

5. *Tartaric acid* added in excess to a very concentrated neutral solution of an ammonia salt, throws down a part of the ammonia as bitartrate of ammonia ($N H_4 O, H O, C_8 H_4 O_{10}$). Dilute solutions are not precipitated. *Bitartrate of soda* precipitates concentrated solutions much more completely, and renders dilute solutions turbid. Bitartrate of ammonia is a white crystalline precipitate. Its for-

mation is facilitated by agitation. It deports itself towards solvents like the corresponding potassa-compound, though it is somewhat more easily dissolved by water and acids.

§ 95.

Recapitulation and remarks.—The salts of potassa and soda are not volatile at a moderate red heat, whilst the salts of ammonia volatilize readily; the latter may therefore be easily separated from the former by ignition. The expulsion of *ammonia* from its compounds, by hydrate of lime, affords the surest means of ascertaining the presence of this substance. Salts of potassa can be detected *positively* only after the removal of the ammoniacal salts which may be present, since both classes of salts manifest the same or a similar deportment with bichloride of platinum and tartaric acid. After the removal of the ammonia, the *potassa* is clearly and positively characterized by either of these two reagents.

It must be remembered that the reactions occur only in concentrated solutions. The operator should therefore evaporate dilute liquids to a small bulk before adding the reagents. One drop of a *concentrated* solution will give at once a decisive result; while no satisfactory indications can be had from any quantity of dilute liquids. The most simple way of detecting the potassa in the two difficultly soluble compounds that have come under our consideration here—viz., the platinchloride of potassium and bitartrate of potassa—is to decompose these salts by ignition; the former, thereupon, yields the potassa in the form of chloride of potassium, the latter in the form of carbonate of potassa. With respect to *soda*, it can be recognized in the humid way with entire certainty, by means of antimonate of potassa, provided that this reagent has been properly prepared, its solution freshly made as directed, § 52, and the soda solution be concentrated, neutral or slightly alkaline in its reaction, and free from other bases save potassa. The antimonate *always* appears crystalline and never flocculent. If, by this test, minute quantities of soda are to be looked for in presence of much potassa, the latter is first precipitated by a slight excess of bichloride of platinum, the platinum is removed from the filtrate by hydrosulphuric acid, the liquid is again filtered, evaporated to dryness, ignited gently, and the residue is dissolved in a very little water, and then the antimonate of potassa is applied.

The coloration which the alkalies impart to the flame, furnishes, however, the most ready and most sensitive means of recognizing them. The unassisted eye is indeed not able to detect potassa in presence of much soda; but, by aid of the indigo-prism or blue glass, the potassa flame is brought out, while the iodide of mercury paper or green glass serves to identify the soda flame.

In the spectroscope the characteristic lines of both alkalies appear at once with such distinctness as to preclude all chances of mistake. [Potassa is masked by much soda.]

[For detecting soda in presence of potassa, antimonate of potassa is somewhat troublesome to prepare and apply. The spectral and flame tests do not always enable the operator to discriminate between accidental traces of soda and such quantities as constitute it an essential or weighable ingredient, of a compound or mixture. A method that supplies this deficiency, is moreover easy of application to very small quantities of substance, and that serves for the simultaneous detection of both alkalies, is the following, described by *J. Lawrence Smith*. The alkali metals must exist as chlorides, and must be free from organic acids or other bases. A small fragment of the solid substance, which need not exceed $\frac{1}{50}$ of an inch in diameter, or a drop of its concentrated aqueous solution, is placed on a slip of glass, and to it is added a single drop of aqueous solution of bichloride of platinum. The plate is now gently warmed; if potassa be present a yellow deposit soon forms, which, under a good magnifier, is seen to consist of octahedral crystals of platinchloride of potassium; the warming is continued until the liquid begins to dry on the edges; if it now be examined with the magnifier the characteristic slender yellow prisms of platinchloride of sodium will be seen. If potassa be present in such quantity that a copious precipitate of platinchloride of potassium separates on addition of bichloride of platinum, it is best to add another drop of the reagent, and allow the precipitate to subside. The liquid is poured off upon another slip of glass, and warmed as above described. When larger quantities of materials are employed, the unassisted eye may usually recognize the crystals of platinchloride of sodium. In looking for minute quantities of soda, recourse must be had to the compound microscope. If the slip of glass be viewed in the microscope by *polarized light*, the reaction becomes extremely sensitive, as the crystals of platinchloride of sodium assume prismatic colors, while those of the potassium salt do not transmit polarized light.

If the beginner fails to find prismatic crystals the first time he evaporates the mixture on the glass slip, he should add a drop of water and repeat the evaporation more slowly. This reaction for soda is uncertain in presence of lithia.]

For the detection of exceedingly minute traces of ammonia a reaction first pointed out by *Nessler* may be employed. Digest at a gentle heat 2 grammes of iodide of potassium, and 3 grammes of iodide of mercury, in 5 cub. cent. of water; add 20 cub. cent. of water, let the mixture stand for some time, then filter; add to the filtrate 30 cub. cent. of pure concentrated solution of potassa (1 : 4); and, should a precipitate form, filter again. If to this solution is added, in small quantity, a liquid containing ammonia or an ammonia-salt, a reddish brown precipitate, or with

exceedingly small quantities of ammonia, a yellow coloration is produced by the formation of hydrated TETRAHYDRARGYRO-IODIDE OF AMMONIUM ($N Hg_4 I + 2 H O$). The chemical interchange is as follows, viz.: $4 (Hg I, K I) + 3 K O + N H_3 = (N Hg_4 I + 2 H O) + 7 K I + H O$. Application of a gentle heat favors its separation. This precipitate redissolves in presence of an excess of ammoniacal salts; but reprecipitates upon further addition of potassa; it is soluble also in solution of iodide of potassium, but the less so the more free potassa happens to be present. When a considerable excess of potassa exists, therefore, the precipitate is insoluble in iodide of potassium. Presence of chlorides of the alkali metals, or of salts of potassa and soda, does not interfere with the reaction; but cyanides and sulphides of the alkali metals prevent it.

[According to *Bohlig*, chloride of mercury is the most sensitive reagent for ammonia, when in the free state or as carbonate. It gives a white precipitate or in very dilute solutions (even when containing but $\frac{1}{200,000}$ of ammonia) a white turbidity due to the separation of CHLORAMIDE OF MERCURY ($Hg Cl + Hg N H_2$). In solutions of the salts of ammonia with other acids than carbonic, a clear solution of mixed carbonate of potassa and chloride of mercury must be employed, which is prepared by adding 10 drops of a solution of the purest carbonate of potassa (§ 78), (1 of salt to 50 of water) and 5 drops of a solution of chloride of mercury (§ 70) to 80 c. c. of water exempt from ammonia (such is the water of many springs, but ordinary distilled water rarely, § 18). This reagent may be kept in closed vessels for a time without change. If much more concentrated, oxide of mercury separates from it. By its use the ammonia salt is first converted into carbonate by double decomposition with the carbonate of potassa, and the further reaction proceeds as before mentioned]

§ 96.

Special Reactions of the rarer Members of the First Group.

1. CÆSIA (Cs O,) and 2. RUBIDIA (Rb O). The compounds of Caesium and Rubidium appear to be widely distributed in nature, though they occur in small quantities. They have been found principally in the mother-liquors of some mineral waters and in some minerals (lepidolite). They have great similarity to the compounds of potassium. Their volatile salts communicate a violet color to the *flame*, and their concentrated aqueous solutions give precipitates with *bichloride of platinum* and *tartaric acid*. Characteristic of these metals is the great insolubility of their platinchlorides. Thus, at 50° Fahr. 100 grm. of water dissolve 900 milligrm. of platinchloride of potassium, but only 154 mgr. of the rubidium- and 50 mgr. of the cæsium-platinchloride. Their *spectra* are especially adapted to their detection, and characterize them most perfectly. The spectrum of cæsium (plate I.) has the pale blue lines α and β of extraordinary brilliancy and definiteness. Next to these in brilliancy is the line γ.

In the spectrum of rubidium the splendid indigo-blue lines α and β are most prominent. Less brilliant though not less characteristic are the deep red lines δ and γ. [Finally, cæsia may be separated from rubidia by converting both into bitartrates and repeatedly recrystallizing these salts from hot solution.—(Allen*). Or better, by uniting them with so much tartaric acid as will form bitartrate of rubidia and neutral tartrate of cæsia, bringing the dried mixture on a funnel and placing it in an atmosphere kept saturated with moisture; tartrate of cæsia deliquesces and passes the funnel, while bitartrate of rubidia remains behind.—(Bunsen)†].

3. LITHIA (Li O), is of frequent occurrence, though usually found in small quantities. It is commonly met with in analyses of mineral waters and the ashes of plants, more rarely in examining minerals, and very seldom in technical analyses.

* American Journal of Science [2] xxxiv. 370. † Pogg. Annalen cxix. 3.

Lithia forms the transition from the first to the second group. It is soluble in water with difficulty, and does not become moist by exposure to the air. Its salts are mostly soluble in water, and some of them (chloride of lithium) are deliquescent. Carbonate of lithia is difficultly soluble, especially in cold water.

Phosphate of soda produces in not too dilute solutions of lithia salts, on boiling, a white crystalline quickly subsiding precipitate of tribasic phosphate of lithia. ($3\,Li\,O\,PO_5$). This characteristic reaction is far more sensitive when the solution of the lithia salt together with phosphate of soda, and so much soda-lye as suffices to maintain an alkaline reaction is evaporated to dryness, the residue softened with water, and an equal volume of solution of ammonia added. In this way very small quantities of lithia may be separated as phosphate. This precipitate fuses before the blowpipe, with carbonate of soda melts to a clear bead; fused on charcoal, it is absorbed by the latter. It dissolves in hydrochloric acid to a solution which remains clear after addition of ammonia in excess; but, on boiling, separates again with its original characters—(Distinction from the alkaline earths.). *Tartaric acid* and *bichloride of platinum* do not affect even concentrated solutions of lithia-salts. When a salt of lithia is brought into the *blowpipe or gas-flame* (§ 14.) the latter is tinged carmine-red. Silicates containing lithia are mixed with sulphate of lime. Phosphate of lithia colors the flame when the fused salt is moistened with hydrochloric acid. The lithia flame is completely masked by that of soda, and when the latter substance is present the flame must be examined by a blue glass or by the thinner parts of the indigo prism. A small quantity of potassa does not disguise the lithia flame. In presence of much potassa, lithia may be detected by comparing through the indigo-prism the flame of the substance to be tested with that of a pure potassa-salt. In this experiment, the two substances are placed near each other on opposite sides of the zone of fusion of the Bunsen lamp. The potassa-lithia flame, viewed through the narrow part of the prism, appears redder in color than the pure potassa flame; at a certain thicker point in the prism both flames appear equally red if the proportion of lithia is very small. If lithia predominates, the intensity of the flame reddened by it, diminishes perceptibly, when seen through the thicker parts of the prism, while the potassa flame is scarcely affected. In this way a few thousandths of lithia may be recognized in salts of potassa. Soda scarcely influences the result unless it is present in very large quantity.—*Cartmell, Bunsen.*

The *spectrum* of lithium (Plate I.) is characterized by the fine carmine-red line α and the faint orange-yellow line β. If chloride of lithium is heated with alcohol and the latter be set on fire, it burns with a magnificent carmine-red color. Soda-salts disguise this reaction.

In order to discover small quantities of caesia, rubidia and lithia when associated with a large amount of potassa and soda, the dry chlorides are extracted with alcohol of 90 per cent. and a few drops of hydrochloric acid, which leaves untouched the greater share of the chlorides of sodium and potassium. The alcoholic solution is evaporated to dryness, the residue is dissolved in a little water and precipitated with bichloride of platinum. The precipitate is repeatedly boiled out with fresh quantities of water, being tested each time in the spectroscope. If rubidia and caesia be present, the spectra of these metals will shortly appear, while that of potassa becomes less marked.

The filtrate from the precipitate of platinchlorides is evaporated to dryness, the residue is gently heated in a current of hydrogen gas in order to decompose platin-chloride of sodium and bichloride of platinum, it is then moistened with hydrochloric acid, dried, and the chloride of lithium is extracted with a mixture of ether and absolute alcohol. This solution, on evaporation, leaves behind chloride of lithium in a nearly pure state, which can be further tested. Before deciding from the simple flame that lithia is present, the dilute aqueous solution of a portion of the supposed chloride of lithium must be examined with carbonate of ammonia to

demonstrate the absence of strontia and lime. The addition of hydrochloric acid before extraction with alcohol is needful, because chloride of lithium on moderate ignition is partially converted into caustic lithia, which, by absorbing carbonic acid from the air, becomes insoluble in alcohol.

§ 97.

SECOND GROUP. ALKALINE EARTHS.

BARYTA, STRONTIA, LIME, MAGNESIA.

Properties of the group.—The alkaline earths in a pure (caustic) state are soluble in water. Magnesia, however, dissolves but very sparingly in water. The solutions manifest alkaline reaction; the alkaline reaction of magnesia is most clearly apparent when that earth is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of the salts of the alkaline earths are therefore precipitated by alkaline carbonates and phosphates. This deportment distinguishes the oxides of the second group from those of the first. They are further distinguished from the oxides of the subsequent groups by not being thrown down from their solutions by hydrosulphuric acid and sulphide of ammonium. The alkaline earths and their salts are colorless, and not volatile at a gentle red-heat; the solutions of their nitrates and chlorides are not precipitated by carbonate of baryta.

Special Reactions.

§ 98.

a. BARYTA (Ba O).

1. CAUSTIC BARYTA is pretty readily soluble in hot water, but rather difficultly so in cold water; it dissolves easily in dilute hydrochloric or nitric acid. HYDRATE OF BARYTA fuses but does not lose its water upon ignition.

2. Most of the SALTS OF BARYTA are insoluble in water. The soluble salts do not affect vegetable colors, and are decomposed upon ignition, with the exception of chloride of barium. The insoluble salts dissolve in dilute hydrochloric acid, except sulphate of baryta and silicofluoride of barium. Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air. Concentrated solutions of baryta are precipitated by hydrochloric or nitric acid added in large proportions, as chloride of barium and nitrate of baryta are not soluble in the aqueous solutions of the said acids.

3 *Ammonia* (free from carbonic acid) produces no precipitate in the aqueous solutions of salts of baryta; *soda* or *potassa* (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of CRYSTALS OF BARYTA (Ba O, H O + 8 aq.) produced by soda or potassa.

4. *Alkaline carbonates* throw down from solutions of baryta CARBONATE OF BARYTA (Ba O, C O_2) in the form of a white precipitate. When carbonate of ammonia is used as the precipitant, or if the solution was previously acid, complete precipitation takes place only upon heating the fluid. In chloride of ammonium the precipitate is soluble to a trifling yet clearly perceptible extent; in very dilute solutions of baryta, therefore, which contain much chloride of ammonium, carbonate of ammonia produces no precipitate.

5. *Sulphuric acid* and all the soluble *sulphates*, also solution of *sulphate of lime*, produce even in very dilute solutions of baryta, a heavy, finely pulverulent, white precipitate of SULPHATE OF BARYTA (Ba O, S O_3), which is insoluble in alkalies, and scarcely soluble in dilute acids; but is perceptibly soluble in boiling concentrated hydrochloric and nitric acids. In strong solutions of ammonia salts, when excess of sulphuric acid is not present, it is also soluble. As a rule, this precipitate is formed immediately upon the addition of the reagent; from highly dilute solutions, however, especially when strongly acid, it separates only after some time.

6. *Hydrofluosilicic acid* throws down from solutions of baryta SILICOFLUORIDE OF BARIUM (Ba Fl_2 + Si Fl_2), in form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; it is perceptibly soluble in hydrochloric and nitric acids. Addition of an equal volume of alcohol hastens the precipitation and makes it so complete that the filtrate remains clear upon addition of sulphuric acid.

7. *Phosphate of soda* produces in neutral or alkaline solutions of baryta a white precipitate of PHOSPHATE OF BARYTA (2 Ba O, H O, P O_5), which is soluble in free acids. Addition of ammonia only slightly increases the quantity of this precipitate, and converts a portion of it into basic phosphate of baryta (3 Ba O, P O_5). Chloride of ammonium dissolves it to a clearly perceptible extent.

8. *Oxalate of ammonia* produces in moderately dilute solutions of baryta a white, pulverulent precipitate of OXALATE OF BARYTA (2 Ba O, C_4 O_6 + 2 aq.) which is soluble in hydrochloric and nitric acids. When recently thrown down, this precipitate dissolves also in oxalic and acetic acids; but the solutions speedily deposit binoxalate of baryta (Ba O, H O, C_4 O_6 + 2 aq.) in the form of a crystalline powder.

9. Soluble pulverized salts of baryta, when heated with dilute *spirit of wine*, impart to the flame a GREENISH YELLOW color, which, however, is not very characteristic.

10. Salts of baryta, when exposed on a platinum wire to the *inner blowpipe flame*, or the *zone of fusion* of the gas lamp, color the flame YELLOWISH-GREEN. The soluble baryta-salts, together with the carbonate and sulphate, give the reaction at once, or after

a little time—phosphate of baryta and silicates decomposable by acids, after moistening with sulphuric or hydrochloric acid. Silicates not decomposable by acids must be fluxed with carbonate of soda, and the carbonate of baryta thus obtained is examined in the flame. The presence of salts of lime and strontia does not prevent the reaction when the sulphates are employed.

11. The baryta flame is characterized by its appearing blue-green when viewed through the *green glass*.

12. The *spectrum* of baryta is figured on Plate I. The green lines α and β are the most intense. Less distinct but still characteristic is the line γ.

13. SULPHATE OF BARYTA is not all or but very slightly decomposed by cold solutions of *alkaline bicarbonates* or of *carbonate of ammonia*. It is also not perceptibly decomposed by a boiling solution of 1 *part of carbonate and* 3 *parts of sulphate of potassa*. Boiling solutions of neutral carbonates of the alkalies, if renewed sufficiently often, decompose it completely. By fusing it with carbonate of soda or potassa, it is easily and perfectly decomposed, there being formed sulphate of the alkali which is soluble, and carbonate of baryta which is insoluble in water.

§ 99.

b. STRONTIA (Sr O).

1. STRONTIA and its HYDRATE and SALTS manifest nearly the same general deportment and properties as baryta and its corresponding compounds.—Hydrate of strontia is more difficultly soluble in water than hydrate of baryta.—Chloride of strontium dissolves in absolute alcohol, and deliquesces in moist air. Nitrate of strontia is insoluble in absolute alcohol, and does not deliquesce in the air.

2. The SALTS OF STRONTIA manifest with *ammonia* and *potassa*, and also with the *alkaline carbonates* and with *phosphate of soda*, nearly the same deportment as the salts of baryta. Carbonate of strontia dissolves somewhat more difficultly in chloride of ammonium than is the case with carbonate of baryta.

3. *Sulphuric acid* and *sulphates* precipitate from solutions of strontia SULPHATE OF STRONTIA (Sr O, S O_3), in form of a white powder. Application of heat greatly promotes the precipitation. Sulphate of strontia is far more soluble in water than sulphate of baryta; owing to this readier solubility, the precipitated sulphate of strontia separates from rather dilute solutions, in general, only after the lapse of some time; and this is invariably the case (even in concentrated solutions) if *solution of sulphate of lime* is used as precipitant. Sulphate of strontia is insoluble in alcohol; addition of the latter, therefore, facilitates its separation. It is perceptibly

soluble in hydrochloric and nitric acids, and the delicacy of this reaction is therefore greatly diminished when these acids are present. The solution of sulphate of strontia in hydrochloric acid is made turbid by chloride of barium, after addition of water.

4. *Hydrofluosilicic acid* fails to produce a precipitate even in concentrated solutions of strontia; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

5. *Oxalate of ammonia* precipitates even from rather dilute solutions, OXALATE OF STRONTIA ($2\ Sr\ O, C_4\ O_6 + 5$ aq.), in form of a white powder, which dissolves readily in hydrochloric and nitric acid, and perceptibly in salts of ammonia, but is only sparingly soluble in oxalic and acetic acid.

6. If salts of strontia soluble in water or alcohol, are heated with dilute spirit of wine, and the latter kindled, the flame appears of an intense CARMINE color, more particularly upon stirring the mixture.

7. Salts of Strontia, when exposed on platinum wire to the *inner blowpipe flame*, or brought into the *zone of fusion* of the gas lamp, impart an intense RED color to the flame. Chloride of strontium gives the strongest reaction. With carbonate and sulphate of strontia the coloration is less intense. The compounds with fixed acids scarcely affect the flame. The substance to be examined is therefore first placed by itself in the flame and afterwards, when moistened with hydrochloric acid, is again subjected to its action. If sulphate of strontia is suspected, it is first exposed a short time to a reducing flame (whereby sulphide of strontium is formed), before it is treated with hydrochloric acid.

8. The strontia flame, viewed through the *blue glass*, appears purple to rose colored, and is hereby distinguished from the lime flame which under the same circumstances has a faint green-gray tint. In presence of baryta the strontia reaction only appears at the moment when the substance moistened with hydrochloric acid is first brought into the flame.

9. The *spectrum* of strontia is represented in Plate I. It contains numerous characteristic lines, especially the orange line, α, the red lines β and γ and the blue line δ. The last is especially adapted for detecting strontia in presence of lime.

10. SULPHATE of STRONTIA is completely decomposed by long digestion with solutions of *carbonate of ammonia* or of *bicarbonates of the alkalies;* also, and far more readily, by boiling with a solution of 1 *part of carbonate and three parts of sulphate of potassa* (important distinction from sulphate of ba[illegible]).

§ 100.

c. Lime (Ca O).

1. Lime and its hydrate and salts present, in their general deportment and properties, a great similarity to baryta and strontia and their corresponding compounds. Hydrate of lime is far more difficultly soluble in water than the hydrates of baryta and strontia; it dissolves, besides, more sparingly in hot than in cold water. Hydrate of lime loses its water upon ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquesce in the air.

2. *Ammonia*, *alkaline carbonates*, and *phosphate of soda*, present nearly the same deportment with salts of lime as with salts of baryta. Recently precipitated carbonate of lime (Ca O, C O_2) is bulky and amorphous—after a time, and immediately upon application of heat, it falls down and assumes a crystalline form. When recently precipitated, it dissolves pretty readily in solution of chloride of ammonium; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in form of crystals.

3. *Sulphuric acid* and *sulphate of soda* produce immediately in very concentrated solutions of lime, white precipitates of sulphate of lime (Ca O, S O_3, H O + aq.), which redissolve completely in a large proportion of water and are still far more soluble in acids. In less concentrated solutions the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solution of sulphate of lime of course cannot produce a precipitate in salts of lime; but even a cold saturated solution of sulphate of potassa, mixed with 3 parts of water, produces a precipitate only after standing from twelve to twenty-four hours. In solutions of lime which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will immediately form upon addition of alcohol.

4. *Hydrofluosilicic acid* does not precipitate salts of lime.

5. *Oxalate of ammonia* produces even in very dilute solutions of lime a white pulverulent precipitate of oxalate of lime. The composition of this precipitate, when thrown down hot or from concentrated solutions, is 2 Ca O, C_4 O + 2 aq; whilst when thrown down cold from dilute solutions, it consists of a mixture of the above salt with 2 Ca O, C_4 O_6 + 6 aq. In very dilute solutions the precipitate forms only after some time. It is readily soluble in hydrochloric and nitric acids, but dissolves to a trifling extent only in acetic and oxalic acids.

6. Soluble salts of lime, when heated with dilute *spirit of wine*, impart to the flame of the latter a yellowish-red color, which is often confounded with that communicated to the flame of alcohol by salts of strontia.

7. Salts of lime when brought into the inner *blowpipe flame* or into the *zone of fusion* of the Bunsen lamp communicate a YELLOW-RED color to the flame. This reaction is most evident with chloride of calcium. Sulphate of lime gives it after it has become basic. Carbonate of lime manifests it most plainly when the carbonic acid has been expelled. Compounds of lime with acids which are not volatile at a high temperature do not tinge the flame; if they are decomposed by hydrochloric acid, the coloration appears after moistening them with this acid. To promote its action, the loop of the platinum wire is flattened with a hammer, a small quantity of the substance is brought upon it and heated until it has caked together, a drop of hydrochloric acid is added, and the whole brought at once into the flame. At the moment when the drop of acid disappears the reaction is most plainly exhibited.—*Bunsen.*

8. Viewed through *green-glass*, the flame obtained as just described, appears siskin-green. This distinguishes it from strontia, which under the same circumstances has a very faint yellow color. *Merz.* In presence of baryta, the reaction is only manifest at the moment when the substance moistened with hydrochloric acid is brought into the flame.

9. The *spectrum* of lime is mapped on Plate I. The bright green line β and the orange line α are the most characteristic. The indigo-blue line at the right of the spectrum is only seen in a good spectroscope.

10. SULPHATE OF LIME manifests the same deportment towards *alkaline carbonates* and *bicarbonates* as sulphate of strontia.

§ 101.

d. MAGNESIA (Mg O).

1. MAGNESIA and its HYDRATE are white powders of far greater bulk than the other alkaline earths and their hydrates. Magnesia and hydrate of magnesia are nearly insoluble both in cold and hot water. Hydrate of magnesia loses its water upon ignition.

2. Some of the SALTS OF MAGNESIA are soluble in water, others are insoluble in that fluid. The soluble salts of magnesia have a nauseous bitter taste; in the neutral state they do not alter vegetable colors; with the exception of sulphate of magnesia, they undergo decomposition when gently ignited, and the greater part of them even upon simple evaporation of their solutions. Sulphate of magnesia loses its acid at a strong white heat. Nearly all the salts of magnesia which are insoluble in water dissolve in hydrochloric acid.

3. *Ammonia* throws down from the solutions of neutral salts of magnesia part of the magnesia as hydrate ($\dot{Mg}O, H O$), in form of a white, bulky precipitate. The rest of the magnesia remains

in solution as a double salt, viz., in combination with the ammoniacal salt which forms upon the decomposition of the salt of magnesia; these double salts are not decomposed by ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds, that ammonia fails to precipitate them in presence of ammoniacal salts in sufficient proportion, or, what is the same, that ammonia produces no precipitate in solutions of magnesia containing a sufficient quantity of free acid; and that precipitates produced by ammonia in neutral solutions of magnesia are redissolved upon the addition of chloride of ammonium.

4. *Soda*, *potassa*, *caustic baryta* and *caustic lime* throw down from solutions of magnesia HYDRATE OF MAGNESIA. The separation of the precipitate is greatly promoted by boiling the mixture. Chloride of ammonium and other similar salts of ammonia redissolve the precipitated hydrate of magnesia if the precipitant has not been added great in excess. If the salts of ammonia are added in sufficient quantity to the solution of magnesia before the addition of the precipitant, small quantities of the latter fail altogether to produce a precipitate. However, upon boiling the solution afterwards with an excess of soda, the precipitate will, of course, make its appearance, since this process causes the decomposition of the ammoniacal salt, removing thus the agent which retains the hydrate of magnesia in solution.

5. *Carbonate of soda* and *carbonate of potassa* produce in neutral solutions of magnesia a white precipitate of BASIC CARBONATE OF MAGNESIA $4\,(Mg\,O,\,CO_2)+Mg\,O\,H\,O+10$ aq. One-fifth of the carbonic acid of the decomposed alkaline carbonate is liberated in the process, and combines with a portion of the carbonate of magnesia to bicarbonate, which remains in solution. This carbonic acid escapes upon ebullition and a further precipitate ($Mg\,O\,C\,O_2+3$ aq.) is produced. Chloride of ammonium and other similar salts of ammonia prevent this precipitation also, and redissolve the precipitates already formed.

6. *Carbonate of ammonia* added to solutions of magnesia does not at once cause a precipitate. After a time, however, except in very dilute solutions, a crystalline precipitate forms, which is a double carbonate of ammonia and magnesia ($N\,H_4\,O,\,CO_2+Mg\,O\,CO_2+4$ aq.) It separates the more rapidly the more concentrated are the solutions. Excess of carbonate of ammonia and free ammonia promote its formation. Chloride of ammonium hinders, but, in concentrated solutions, cannot altogether prevent its separation.

7. *Phosphate of soda* precipitates from solutions of magnesia, if they are not too dilute, PHOSPHATE OF MAGNESIA ($2\,Mg\,O,\,H\,O,\,P\,O_5+14$ aq.) as a white powder. On boiling, basic phosphate of magnesia ($3\,Mg\,O,\,P\,O_5+7$ aq.) is formed which separates even

from quite dilute solutions. But if the addition of the precipitant is preceded by that of chloride of ammonium and ammonia, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA (2 Mg O, N H, O, P O_5+12 aq.) will separate, even from very dilute solutions of magnesia; its separation may be greatly promoted and accelerated by vigorous stirring with a glass rod: even should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the side of the vessel will, after the lapse of some time, appear distinctly as white streaks. Water and solutions of salts of ammonia dissolve the precipitate but very slightly; but it is readily soluble in acids, even in acetic acid. In water containing ammonia it is as good as insoluble.

8. *Oxalate of ammonia* produces no precipitate in highly dilute solutions of magnesia; in less dilute solutions no precipitate is formed at first, but after some time crystalline crusts of various oxalates of ammonia and magnesia make their appearance. In highly concentrated solutions oxalate of ammonia very speedily produces precipitates of oxalate of magnesia (2 Mg O, C_4 O_6+4 aq.), which contain small quantities of the above-named double salts. Chloride of ammonium, especially in presence of free ammonia, interferes with the formation of these precipitates; but, as a rule, it does not absolutely prevent it.

9. *Sulphuric acid* and *hydrofluosilicic acid* do not precipitate salts of magnesia.

10. If magnesia, or a salt of magnesia, is moistened with water, heated to redness on a charcoal support, then moistened with 1 drop of solution of *nitrate of protoxide* of cobalt, and again heated at first to gentle redness, ultimately to intense redness, in the oxidation flame, a pinkish mass is obtained, the color of which becomes distinctly apparent only upon cooling, but is never very intense. Alkalies, alkaline earths, and heavy metallic oxides prevent the reaction.

11. Salts of magnesia impart no coloration to the *flame*.

§ 102.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the ready solubility of the sulphate, and the disposition of salts of magnesia to form double salts with ammoniacal compounds, are the three principal points in which magnesia differs from the other alkaline earths. To detect magnesia we always first remove the baryta, strontia, and lime, if these bodies happen to be present.

This is accomplished most conveniently (because the latter bases are at the same time procured in the form best adapted for further examination) by precipitating with carbonate of ammonia with addition of some caustic ammonia and chloride of ammonium, and

gently heating. If the solutions are moderately dilute and the precipitate is shortly brought upon a filter, it consists of carbonates of baryta, strontia, and lime, while all the magnesia remains in solution and is found in the filtrate. Since, however, chloride of ammonium dissolves carbonate of baryta and even carbonate of lime to some, though but a slight extent, small quantities of these bases pass into the filtrate, and when but traces of them are present they may remain entirely in solution.

In exact investigations it is therefore advisable to divide the filtrate into three portions, in one of which any dissolved *baryta* is detected by dilute sulphuric acid, while the second is tested for *lime* by means of oxalate of ammonia. In case these reagents produce no turbidity, even after the lapse of some time, the third portion is examined for *magnesia* by means of phosphate of soda. If, on the other hand, a precipitate appears in either of the first two portions, it is filtered off after it has completely subsided, and the filtrate is tested for *magnesia*. If both the first and second portions are turbid they are mixed together, after some time are filtered, and the filtrate is tested with phosphate of soda. To prove that a precipitate produced by oxalate of ammonia is really oxalate of lime, and not an oxalate of ammonia and magnesia, it is dissolved in a little hydrochloric acid, and a few drops of dilute sulphuric acid and some alcohol are added, when sulphate of lime should separate, if *lime* were present.

The precipitate by carbonate of ammonia may be examined for baryta, strontia, and lime, as follows:

It is dissolved, after washing, in dilute hydrochloric acid. To a small portion of the liquid, solution of sulphate of lime is added; an immediate precipitate is proof of the presence of BARYTA. The rest of the hydrochloric solution is evaporated to dryness and the residue is treated with absolute alcohol (§ 19). Chloride of barium mostly remains undissolved while the chlorides of strontium and calcium enter into solution. The alcoholic solution is mixed with an equal volume of water and some drops of hydrofluosilicic acid; the last traces of baryta are thus thrown down if the mixture is allowed to stand for several hours. To the alcoholic filtrate, sulphuric acid is added which precipitates from it strontia and lime. The precipitated sulphates are collected on a filter, washed with weak alcohol [4 volumes of alcohol of 92 per cent. mixed with 5 volumes of water], and converted into carbonates by boiling with solution of carbonate of soda. The carbonates thus obtained are well washed with water, dissolved in a little hydrochloric acid, the solution is evaporated to dryness, and the residue is taken up by a little water. The aqueous solution is filtered, if necessary, and divided into two portions. To one of these, solution of sulphate of lime is added; a precipitate formed after some time, it may be

a long time, indicates STRONTIA. The other portion is treated with solution of sulphate of potassa, heated to boiling and filtered, to remove strontia. The filtrate from the sulphate of strontia is tested with oxalate of ammonia for LIME. In precipitating strontia by sulphate of potassa, a portion of the lime may also be separated if it is present in large quantity, but enough always remains in the filtrate to detect with certainty.

The best way of detecting the alkaline earths, when in the form of *phosphates*, is to decompose these latter by means of sesquichloride of iron with the addition of acetate of soda (§ 145). The *oxalates* of the alkaline earths are converted into carbonates by ignition, preparatory to the detection of the individual earths which they contain.

A mixture of the *sulphates* of the alkaline earths is first washed with small quantities of boiling water. All the *sulphate of magnesia* and a small quantity of sulphate of lime thus pass into solution. The residue, which must be finely pulverized, is digested, as *Rose* recommends, for 12 hours in a cold solution of carbonate of ammonia, or is boiled 10 minutes in a solution of one part of carbonate and three parts of sulphate of potassa, thrown on a filter, thoroughly washed, and then treated with dilute hydrochloric acid, which dissolves the carbonates of lime and strontia, and likewise a slight trace of baryta (*Fresenius*); but leaves behind *sulphate of baryta*. The latter can be decomposed by fusion with carbonate of soda. The solutions thus obtained are to be further tested as previously directed.

By aid of the spectroscope, baryta, strontia, and lime may be detected, even when occurring together, far more easily than by following the highly instructive but somewhat tedious processes of the humid method. The substance under examination is brought into the flame of the gas-lamp, either directly or after moistening with hydrochloric acid.

[Minute quantities of baryta and strontia give no spectral lines in presence of much lime. *Engelbach* directs that the mixed carbonates be strongly ignited by means of a blast-lamp for a few minutes, whereby, in presence of carbonate of lime, baryta and strontia readily become caustic. The mass is extracted with a little distilled water, the solution evaporated to dryness with hydrochloric acid and the residue examined in the spectroscope.]

The earths just named may also be severally recognized in their mixtures, without the spectroscope, by observing the coloration they impart to the flame. The substance is repeatedly moistened with sulphuric acid and cautiously dried. It is then brought into the *zone of fusion* of the gas flame. After any alkalies that may be present in the mixture have volatilized, the baryta coloration appears by itself. (§ 98, 10.)

After it has entirely disappeared, and the substance on moistening with hydrochloric acid gives, at the moment when the latter evaporates, no more a flame, that seen through the green glass appears blue-green, the substance is again moistened with hydrochloric acid, and its flame examined by help of the green glass (§100, 8), for lime, and with the blue glass for strontia.—*Merz.*

§ 103.

THIRD GROUP.

Of common occurrence: ALUMINA, SESQUIOXIDE OF CHROMIUM.

Of rare occurrence: GLUCINA, THORIA, ZIRCONIA, YTTRIA, TERBIA, ERBIA, OXIDES OF CERIUM, LANTHANUM, DIDYMIUM; TITANIC, TANTALIC, AND HYPONIOBIC ACIDS:

Properties of the group.—The oxides of the third group are insoluble in water, both in the pure state and as hydrates. Their sulphides cannot be produced in the humid way. Hydrosulphuric acid therefore fails to precipitate their solutions. From salts in which the oxides of the third group play the part of base,* sulphide of ammonium as well as ammonia, throws down the hydrated oxides. This deportment with sulphide of ammonium distinguishes the oxides of the third from those of the two preceding groups.

Special Reactions of the more commonly occurring Oxides.

§ 104.

a. ALUMINA (Al_2O).

1. ALUMINUM is a nearly white metal. It undergoes no oxidation on exposure to the air, and when massive scarcely oxidizes on ignition. It is very malleable and may be wrought by the file. Its sp. gr. is but 2.56. It fuses at a bright red heat. The finely divided, but not the compact metal, decomposes water at a boiling heat. Aluminum dissolves easily in hydrochloric acid as well as in hot soda-lye, with evolution of hydrogen. It is but slowly dissolved even by hot nitric acid.

2. ALUMINA is non-volatile and colorless; the HYDRATE is also colorless. Alumina dissolves in acids (particularly when dilute) slowly and with very great difficulty; in fusing bisulphate of potassa it dissolves readily to a mass soluble in water. The hydrate in an amorphous state, and recently precipitated, is readily soluble in acids; but after being left some time in the fluid

* The oxides of the third group are mostly capable of uniting with acids as well as with bases to produce saline compounds, *e. g.* alumina unites with potassa forming aluminate of potassa, and with sulphuric acid yields sulphate of alumina. These oxides, therefore, stand in part on the boundary between bases and acid. Those which most nearly agree in character with the latter are designated as acids.

from which it was precipitated, its solubility decreases, and in the crystallized state it dissolves with very great difficulty in acids. After previous ignition with alkalies, which leads to the formation of aluminates of the alkalies, alumina is readily dissolved by acids.

3. The SALTS OF ALUMINA are mostly colorless, and non-volatile: some of them are soluble, others insoluble. Anhydrous chloride of aluminum is a yellow crystalline volatile solid. The soluble salts have a sweetish astringent taste, redden litmus paper, and lose their acids upon ignition. The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds. The compounds of alumina which are insoluble in hydrochloric acid are decomposed and made soluble by ignition with carbonate of soda and potassa, or bisulphate of potassa. They may also be decomposed and brought into solution by heating for two hours at a temperature of 390° to 410° Fah. with hydrochloric acid of 25 *per cent.* or with a mixture of three parts of hydrated sulphuric acid and 1 part of water. The substance must be in a state of fine division. The heating is performed in a sealed glass tube. —(*A. Mitscherlich.*)

4. *Soda* and *potassa* throw down from solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA ($Al_2 O_3$, 3 H O), which contains alkali, and generally also an admixture of basic salt; this precipitate re-dissolves readily and completely in an excess of the precipitant, but from this solution it is reprecipitated by addition of chloride of ammonium, even in the cold, but more completely upon application of heat (compare § 54). The presence of salts of ammonia does not prevent the precipitation by potassa or soda.

5. *Ammonia* also produces in solutions of alumina a precipitate of HYDRATE OF ALUMINA, containing ammonia and an admixture of basic salt; this precipitate also redissolves in a very considerable excess of the precipitant, but with difficulty only, which is the greater the larger the quantity of salts of ammonia contained in the solution. It is this deportment which accounts for the complete precipitation of hydrate of alumina from solution in potassa, by an excess of chloride of ammonium.

6. *Carbonates of the alkalies* throw down from solutions of alumina BASIC CARBONATE OF ALUMINA, which is insoluble or but very slightly soluble in excess of the precipitant.

7. If the solution of a salt of alumina is digested with finely pulverized carbonate of baryta, the greater part of the acid of the alumina salt combines with the baryta, the liberated carbonic acid escapes, and the alumina precipitates completely as HYDRATE mixed with BASIC SALT OF ALUMINA; even digestion in the cold suffices to produce this reaction.

8. If alumina or one of its compounds is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of

nitrate of protoxide of cobalt, and then again strongly ignited, an unfused mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candlelight it appears violet. This reaction is decisive only in the case of infusible or difficultly fusible compounds of alumina pretty free from other oxides, as solution of cobalt imparts a blue tint to readily fusible salts, even though no alumina be present.

§ 105.

b. SESQUIOXIDE OF CHROMIUM ($Cr_2 O_3$).

1. SESQUIOXIDE OF CHROMIUM is a green, its HYDRATE a bluish gray-green powder. The hydrate dissolves readily in acids; the non-ignited sesquioxide dissolves more difficultly, and the ignited sesquioxide is almost altogether insoluble.

2. The SALTS OF SESQUIOXIDE OF CHROMIUM have a green or violet color. Many of them are soluble in water. Most of them dissolve in hydrochloric acid. The solutions exhibit either a fine green or a deep violet color; the latter, however, acquire a green tint when even moderately heated. The salts of sesquioxide of chromium with volatile acids are decomposed upon ignition, the acids being expelled. The salts of sesquioxide of chromium which are soluble in water redden litmus. Anhydrous sesquichloride of chromium is crystalline, difficultly volatile, insoluble in water and acids, and of a fine violet color.

3. *Potassa and soda* produce in solutions, both of the green and violet salts of sesquioxide of chromium, a bluish-green precipitate of HYDRATE OF SESQUIOXIDE OF CHROMIUM, which dissolves readily and completely in an excess of the precipitant, imparting to the fluid an emerald-green tint. Upon *long-continued* ebullition of this solution, the whole of the hydrated sesquioxide separates again, and the supernatant fluid appears perfectly colorless. The same reprecipitation takes place if chloride of ammonium is added to the alkaline solution, and the mixture heated.

4. Ammonia precipitates from the green solutions of sesquioxide of chromium grayish-green, from the violet solutions, grayish-blue, HYDRATE OF SESQUIOXIDE OF CHROMIUM. The former precipitate dissolves in acids with a green, the latter with a violet color. The color and composition of these precipitates is influenced by various circumstances; viz., the concentration of the solutions, the mode in which the precipitant is added, &c. A small portion of these hydrates may redissolve in an excess of the precipitant in the cold, imparting to the fluid a peach-blossom red tint; but if, after the addition of ammonia in excess, heat is applied to the mixture, the precipitation is complete.

5. Carbonates of the alkalies precipitate BASIC CARBONATE OF SESQUIOXIDE OF CHROMIUM, which is soluble in a large excess of the precipitant.

6. *Carbonate of baryta* precipitates from solutions of sesquioxide of chromium the whole of the sesquioxide as a GREENISH HYDRATE mixed with BASIC SALT. The precipitation takes place in the cold, but is complete only after long-continued digestion.

7. If the solution of sesquioxide of chromium in soda or potassalye is boiled a short time with an excess of *binoxide of lead*, the sesquioxide of chromium is converted into chromic acid. On filtering, a yellow fluid is obtained, which holds chromate of lead in solution, and upon supersaturation with acetic acid, CHROMATE OF LEAD separates in form of a yellow precipitate.—(*Chancel.*) Minute traces of chromic acid may be detected in the alkaline solution with more certainty by acidifying it by means of hydrochloric acid, and adding binoxide of hydrogen and ether. Compare chromic acid (§ 141, 8).

8. The fusion of sesquioxide of chromium or of any of its compounds with *nitrate of soda and some carbonate of soda* gives rise to the formation of yellow CHROMATE OF SODA, part of the oxygen of the nitric acid separating from the nitrate of soda, and converting the sesquioxide of chromium into chromic acid, which then combines with the soda. For the reactions of chromic acid, see § 141.

9. *Phosphate of soda and ammonia* dissolves sesquioxide of chromium and its salts, both in the *oxidizing* and *reducing* flame of the blowpipe or Bunsen's lamp, to clear beads of a faint YELLOWISH-GREEN tint, which upon cooling change to EMERALD-GREEN. The sesquioxide of chromium and its salts show a similar deportment with *biborate of soda.*

§ 106.

Recapitulation and remarks.—The solubility of hydrate of alumina in solutions of potassa and soda, and its reprecipitation from the alkaline solutions by chloride of ammonium, afford a safe means of detecting alumina only in the absence of sesquioxide of chromium. If the latter is present, therefore, which is seen either from the color of the solution, or by the reaction with phosphate of soda and ammonia, it must be removed before we can proceed to test for alumina. The separation of sesquioxide of chromium from alumina is effected the most completely by fusing 1 part of the mixed oxides together with 2 parts of carbonate and 2 parts of nitrate of soda, which may be done in a platinum crucible. The yellow mass obtained is boiled with water; by this process the whole of the chromium is dissolved as chromate of soda, and part of the alumina as aluminate of soda, the rest of the alumina remain-

4. YTTRIA (Y O) is met with in the rare minerals gadolinite, orthite, and yttrotantalite. The ignited earth is easily dissolved by hydrochloric acid (distinction from zirconia and thoria). When pure it is white, but when it contains erbia and terbia has a brownish-yellow color. Its hydrate is white, attracts carbonic acid from the air, when freshly precipitated is soluble in boiling solution of chloride of ammonium (distinction from alumina and zirconia). The salts of yttria are white with an amethystine tinge. Anhydrous chloride of yttrium is not volatile (distinction from alumina, glucina, thoria, and zirconia)—*Potassa* throws down white hydrate which is insoluble in excess (distinction from alumina and glucina). *Ammonia* and *sulphide of ammonium* act like potassa. A small amount of chloride of ammonium does not prevent the precipitation by ammonia and sulphide of ammonium; but in presence of a large excess of this salt no precipitate is produced.

Carbonates of the alkalies give a white precipitate, which dissolves with difficulty in carbonate of potassa, more easily in bicarbonate of potassa and in carbonate of ammonia (but not to nearly the same extent as carbonate of glucina). The solution of pure hydrate of yttria in carbonate of ammonia deposits all its yttria on boiling. If, however, chloride of ammonium be present, the precipitate redissolves on further heating with separation of ammonia and formation of chloride of yttrium. It is to be observed further, that from saturated solutions of carbonate of yttria in carbonate of ammonia, double carbonate of yttria and ammonia readily separates. *Oxalic acid* gives a white precipitate (distinction from alumina and glucina). This precipitate is insoluble in oxalic, but soluble in hydrochloric acid. *Sulphate of potassa* precipitates double sulphate of yttria and potassa, which is soluble, though slowly, in much water even when it has been thrown down from hot solutions (distinction from zirconia); it is somewhat more soluble in solution of sulphate of potassa (distinction from thoria), and still more soluble in solutions of salts of ammonia. *Carbonate of baryta* does not precipitate yttria even on boiling. *Turmeric paper* is not affected by the acidified solutions of yttria (distinction from zirconia).—*Tartaric acid* does not prevent the precipitation by alkalies (characteristic distinction from alumina, glucina, thoria, and zirconia). The precipitate is tartrate of yttria. The precipitation takes place only after the lapse of some time; it is, however, complete.

5. TERBIA (Tr O) and 6 ERBIA (E O). These oxides usually accompany yttria. Gradual addition of ammonia to a solution of the three bases first throws down erbia, then terbia, and lastly yttria. Erbia after ignition is yellow or orange-yellow in color. Terbia appears to be white, though it is not known in the pure state. No further means of distinguishing these earths, or separating them from each other, are known.

7. OXIDES OF CERIUM.—Cerium occurs as protoxide in the rare minerals, cerite, orthite, &c. It forms two oxides, the protoxide (Ce O), and the sesquioxide ($Ce_2 O_3$). The hydrated protoxide is white; exposed to the air it absorbs oxygen and becomes yellow; ignited in the air it passes into orange-red or red sesquioxide (distinction from the previously described earths). The hydrated protoxide easily dissolves in acids. The ignited sesquioxide, when it contains oxides of lanthanum and didymium, dissolves easily in hydrochloric acid with evolution of chlorine; when pure, sesquioxide of cerium is scarcely soluble in boiling hydrochloric acid; on addition of alcohol it, however, dissolves (distinction from thoria and zirconia); the solution contains protochloride of cerium. The salts of protoxide of cerium are colorless, sometimes with an amethystine tinge; those which are soluble redden litmus. Protochloride of cerium is not volatile (distinction from alumina, glucina, thoria and zirconia). Cerite (hydrous silicate of protoxide of cerium, (Ce O, La O, Di O)$_2$ S. $O_3 + 2$ aq) is insoluble in aqua regia, is, however, decomposed by fusion with carbonate of soda, and by digestion with concentrated sulphuric acid. *Potassa* precipitates from solutions of protoxide of cerium white hydrate, which turns yellow in the air, and is insoluble in excess of the precipitant (distinction from alumina and

glucina). *Ammonia* throws down a basic salt insoluble in excess. *Carbonates of the Alkalies* give white precipitates slightly soluble in excess of carbonate of potassa, more easily soluble in carbonate of ammonia.—*Oxalic acid* precipitates protoxide of cerium completely, even from moderately dilute solutions (distinction from alumina and glucina). The precipitate is insoluble in oxalic acid, but is taken up by a large quantity of hydrochloric acid. A saturated solution of *sulphate of potassa* throws down, even from somewhat acid solutions, white double sulphate of potassa and protoxide of cerium (distinction from alumina and glucina), which is very difficultly soluble in water, and totally insoluble in a saturated solution of sulphate of potassa (distinction from yttria). This precipitate may be dissolved in a large quantity of boiling water to which some hydrochloric acid is added. *Carbonate of baryta* precipitates cerium slowly but completely. *Tartaric acid* prevents the precipitation by ammonia (distinction from yttria), but not by potassa. *Borax* and *microcosmic salt* dissolve cerium in the outer flame to red beads (distinction from the previously mentioned earths), the color fades or even disappears on cooling. In the inner flame the beads are colorless.

8. OXIDE OF LANTHANUM is usually associated with protoxide of cerium. It is white, and does not change color on ignition (distinction from protoxide of cerium); in contact with cold water it is slowly, by hot water rapidly, converted into milk-white hydrate. The oxide and its hydrate both turn red litmus paper blue, and are dissolved by boiling solution of chloride of ammonium, and by dilute acids; oxide of lanthanum thus resembles magnesia. The salts are colorless; the saturated solution of sulphate of lanthanum in cold water, deposits a portion of the salt upon heating to 86° F. (distinction from protoxide of cerium). *Sulphate of potassa, oxalic acid, and carbonate of baryta* react as has been described under cerium. *Potassa* throws down hydrate, which is insoluble in excess, and does not turn brown on exposure to the air. *Ammonia* precipitates basic salts, which, when washed, run milky through the filter. The precipitate by *carbonate of ammonia* is entirely insoluble in excess of this reagent (distinction from Ce O). By supersaturating the solution of acetate of lanthanum with ammonia, washing the precipitate several times with cold water and adding a little powdered iodine, a blue color gradually pervades the mass (characteristic distinction of lanthanum from all the other earths).

9. OXIDE OF DIDYMIUM occurs together with cerium and lanthanum, white after strong ignition; moistened with nitric acid and gently ignited, dark brown; becomes white again on strong ignition. In contact with water, slowly passes into hydrate; absorbs carbonic acid; is destitute of alkaline reaction; dissolves easily in acids. Its strong solutions have a reddish or faintly violet color. The saturated solution of the sulphate is not precipitated by heating to 86° F., but, on boiling, salt is deposited. *Potassa* throws down hydrated oxide that does not alter when exposed to the air, and is insoluble in excess of the precipitant. *Ammonia* precipitates basic salts which are insoluble in ammonia, but somewhat soluble in chloride of ammonium. *Alkaline carbonates* give copious precipitates which are insoluble in excess, even of carbonate of ammonia (distinction from protoxide of cerium), but are somewhat soluble in chloride of ammonium. *Oxalic acid* precipitates oxide of didymium almost completely; the precipitate is soluble with difficulty in cold, with ease in hot hydrochloric acid. *Carbonate of baryta* throws down oxide of didymium very slowly (more slowly than protoxide of cerium, and oxide of lanthanum), and never completely. Salts of didymium are more slowly and less completely precipitated by *sulphate of potassa* than salts of protoxide of cerium. The precipitate is insoluble in cold, and difficultly soluble in hot hydrochloric acid. *Microcosmic salt* dissolves oxide of didymium in the reduction flame to a violet amethyst bead; with soda in the outer flame a grayish mass is obtained (distinction from manganese).

Entirely satisfactory methods of separating the oxides of cerium, lanthanum, and didymium from each other are not known. Sesquioxide of cerium is obtained nearly

pure as a residue, when the mixed oxides are ignited in the air and afterwards treated with concentrated nitric acid. This process is repeated with the nitric acid solution, whereby nearly all the cerium is removed from it. From the solution, the oxides of lanthanum and didymium are thrown down by an alkali, washed and dissolved in sulphuric acid. Water at a temperature of 41° to 43° Fah., is now saturated with the dry sulphates. The saturated solution is finally heated to 86° Fah. when sulphate of lanthanum separates, while sulphate of didymium remains in solution.

10. TITANIC ACID.—Titanium forms two oxides; the sesquioxide ($Ti_2 O_3$) and titanic acid ($Ti O_2$). The latter is most frequently met with. It occurs free in rutile and anatase, combined in titanite, titanic iron, &c. It is found in small quantity in many iron ores, and in the slags of iron furnaces. The small copper-red cubic crystals, sometimes seen in iron slags, are cyano-nitride of titanium. Gently ignited titanic acid is white, and when heated, transiently assumes a yellow color. When strongly ignited it is yellowish or brownish. It is infusible, insoluble in water, has a sp. gr. of 3.9 to 4.25.

a. Deportment of titanic acid to acids, and reactions of its acid solutions. Ignited titanic acid is insoluble in acids with exception of hydrofluoric acid and strong sulphuric acid. Heated sufficiently long with bisulphate of potassa, it dissolves to a clear mass which is taken up by a considerable quantity of water, forming a clear solution. Hydrated titanic acid when moist, or when dried at ordinary temperatures, is soluble in dilute acids, especially hydrochloric and sulphuric. From all the solutions of titanic acid in hydrochloric or sulphuric acids, when highly diluted, especially from the last, the titanic acid separates *on long continued boiling*, as a white powder insoluble in dilute acids. Much free acid hinders the precipitation and diminishes the quantity of the precipitate. The titanic acid thus separated from its solution in hydrochloric acid may be collected on a filter, but runs through on washing, unless hydrochloric acid or chloride of ammonium be added. *Potassa* throws down from the hydrochloric or sulphuric solution of titanic acid, a voluminous white precipitate of hydrated titanic acid, which is insoluble in excess of the precipitant. The same effect is produced by *ammonia, sulphide of ammonium, carbonates of the alkalies*, and *carbonate of baryta*. The precipitate when thrown down in the cold, and after washing with cold water, is soluble in dilute hydrochloric and sulphuric acids. Tartaric acid prevents its formation. *Ferrocyanide of potassium* gives with acid solutions of titanic acid, a dark brown precipitate; *tincture of galls*, a precipitate which is brownish at first, but shortly changes to orange-red. Zinc reduces titanic acid in acid solutions to sesquioxide of titanium, causing at first a blue coloration of the liquid, and finally the separation of blue hydrated sesquioxide.

b. Behavior of titanic acid to alkalies. Freshly precipitated hydrated titanic acid is scarcely soluble in solution of potassa. If titanic acid be fused with *hydrate of potassa*, and treated with water, the alkaline liquid contains somewhat more titanic acid. Fused with *carbonate of potassa or soda*, carbonic acid is expelled and neutral titanate of the alkali is formed. On treating the fused mass with water, carbonate and hydrate of the alkali are dissolved and an acid titanate remains behind. The latter is soluble in hydrochloric acid. When titanic acid is mixed with charcoal, and ignited in a stream of *chlorine gas*, liquid, volatile and fuming chloride of titanium is produced. *Microcosmic salt* dissolves titanic acid with ease in the outer flame to a clear bead, which is yellowish while hot and colorless when cold. In a good reducing flame (more easily on addition of some metallic tin) the bead becomes yellow when hot, red when somewhat cooled, and violet when cold. If sulphate of iron be added the bead obtained in the inner flame is blood-red.

11. TANTALIC ACID.—There are two oxides of Tantalum, viz., $Ta O_2$ and $Ta O_5$. The last—tantalic acid—exists in tantalite, yttrotantalite and some other rare mine-

rals. It is white and remains so after ignition (distinction from titanic acid). The ignited Ta_2O_5 has a density of 7 to 8. Tantalic acid unites both to acids and bases.

a. Deportment to acids. The ignited acid is dissolved neither by hydrochloric acid nor even by strong sulphuric acid. It fuses together with bisulphate of potassa. On treating the fused mass with water the tantalic acid remains behind, combined with sulphuric acid (distinction, but imperfect separation from TiO_2). The sulphate of tantalic acid is converted into pure Ta_2O_5 by ignition in an atmosphere of carbonate of ammonia. If the solution of an alkaline tantalate has added to it excess of hydrochloric acid, the precipitate which forms at first afterwards dissolves to an opaline liquid Out of this solution *ammonia* and *sulphide of ammonium* throw down hydrated tantalic acid, or acid tantalate of ammonia; the precipitation is prevented by tartaric acid. *Sulphuric acid* throws down from the opaline solution sulphate of tantalic acid. When tantalates of the alkalies are strongly acidified with hydrochloric acid and put in contact with *zinc*, there ensues little or no blue coloration, even on further addition of sulphuric acid; if, however, solid chloride of tantalum be dissolved in strong sulphuric acid, and water and zinc be added, the liquid acquires a blue color, which on standing does not change to brown.

b. Behavior towards alkalies. Tantalic acid, when long fused with *hydrate of potassa*, forms tantalate of potassa, which dissolves in water. Fused with *hydrate of soda*, it gives a turbid mass; when this is treated with a little water all the tantalic acid remains as tantalate of soda, this salt being insoluble in solution of soda; it dissolves, however, in water as soon as the excess of soda is removed. From the aqueous solution it is thrown down again in a crystalline state by gradual addition of soda lye. *Carbonic acid* throws down from solutions of alkaline tantalates acid salts, which do not dissolve when boiled with solution of carbonate of soda. *Sulphuric acid* throws down, even from dilute solutions of alkaline tantalates, sulphate of tantalic acid. *Ferrocyanide of potassium* and *tincture of galls* precipitate these solutions only on acidifying them. The former gives a yellow, the latter a light brown precipitate.

Ignited with charcoal in a stream of *chlorine gas*, tantalic acid yields a yellow, solid chloride of tantalum, which forms a crystalline sublimate; if the tantalic acid contain titanic acid, the fuming chloride of titanium appears at the same time; *Microcosmic salt* dissolves tantalic acid to a colorless bead both in the inner and outer flames. It is not made blood-red by addition of sulphate of iron (distinction from titanic acid).

12. HYPONIOBIC ACID. Niobium (Columbium) forms with oxygen two compounds—hyponiobic and niobic acids. (Nb_2O_5 and NbO_2) The first occurs in a few rare minerals as columbite, samarskite, &c. It is white, on ignition is transiently yellow (distinction from tantalic acid). Its density is 4.6 to 6.5 (distinction from tantalic acid). The hyponiobic acid combines both with bases and acids.

a. Acid solutions. Hyponiobic acid is dissolved by hot concentrated sulphuric acid. On addition of much cold water a clear liquid is obtained from which sulphate of hyponiobic acid is precipitated gradually in the cold and quickly on boiling. By washing this precipitate with solution of carbonate of ammonia, and finally with very dilute hydrochloric acid, hydrated hyponiobic acid—by igniting in an atmosphere of carbonate of ammonia, anhydrous hyponiobic acid is obtained. *Ammonia* and *sulphide of ammonium* throw down from the solutions, acid hyponiobate of ammonia.—Bisulphate of potassa in fusion easily dissolves the acid; on treating the fused mass with hot water sulphate of hyponiobic acid remains behind.

b. Alkaline solutions. With caustic potassa the acid readily fuses to a clear mass, soluble in water. With caustic soda the fused mass is turbid; water first extracts from it the excess of soda, leaving hyponiobate of soda which dissolves in pure water. The carbonate of soda gives, on fusion, similar results. Crystallized hypo-

niobate of soda is obtained by gradually adding soda-lye to its aqueous solution. Solutions of the hyponiobates are not rendered turbid by boiling. *Sulphuric acid* throws down from them, on boiling, all the hyponiobic acid. *Chloride of ammonium* precipitates them less completely. *Hydrochloric acid* gives a precipitate which is insoluble in excess (distinction from titanic and tantalic acids). The separated hyponiobic acid in presence of hydrochloric acid gives with *zinc* at first a blue and afterwards a brown color (distinction from tantalic acid). *Carbonic acid* throws down acid hyponiobates of the alkalies which are soluble in boiling dilute solution of carbonate of soda (separation from tantalic acid). In alkaline solutions, *ferrocyanide of potassium* and *tincture of galls* have no effect; on acidifying the liquids, the former gives a dark brown, the latter a deep orange-red precipitate. On heating the acid mixed with charcoal in a stream of *chlorine gas*, there are obtained white solid $Nb_2 Cl_3$ and yellow solid but more volatile $Nb Cl_2$.—*Microcosmic salt* dissolves the acid copiously, the bead obtained in the inner flame has a violet blue or brown color, according to the quantity of hyponiobic acid added and the mode of its preparation; with sulphate of iron the bead becomes red.

The mode of proceeding to detect most and perhaps all the oxides of the third group in presence of each other is considered in Section III. Part II.

§ 108.

FOURTH GROUP.

OF COMMON OCCURRENCE: OXIDE OF ZINC, PROTOXIDE OF MANGANESE, PROTOXIDE OF NICKEL, PROTOXIDE OF COBALT, PROTOXIDE OF IRON, SESQUIOXIDE OF IRON.

OF RARE OCCURRENCE: OXIDES OF URANIUM, OXIDES OF VANADIUM, OXIDES OF THALLIUM.

Properties of the group.—The solutions of the oxides of the fourth group, when containing a stronger free acid, are not precipitated by hydrosulphuric acid; neutral solutions also are not, or only very incompletely, precipitated by that reagent; but alkaline solutions are completely precipitated by hydrosulphuric acid; and so are other solutions if a sulphide of an alkali-metal is used as the precipitant, instead of hydrosulphuric acid. The precipitated metallic sulphides corresponding to the respective oxides are insoluble in water; some of them are readily soluble in dilute acids; others (sulphide of nickel and sulphide of cobalt) dissolve only with very great difficulty in these menstrua. Some of them are insoluble in sulphides of the alkali metals; others are sparingly soluble in them, under certain circumstances (nickel) or completely soluble (vanadium).

The oxides of the fourth group are therefore distinguished from those of the first and second groups by the fact that their solutions are precipitated by sulphide of ammonium; from those of the third group by the circumstance that they are thrown down by this reagent as sulphides, and not, as is the case with alumina, &c., as hydrated oxides.

Special Reactions of the more commonly occurring Oxides.

§ 109.

a. OXIDE OF ZINC (Zn O).

1. METALLIC ZINC is bluish-white and very bright; when exposed to the air, a thin coating of basic carbonate of zinc forms on its surface. It is of medium hardness, ductile at a temperature of between 212° and 302° Fah., and under ordinary circumstances more or less brittle; it fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Zinc dissolves in hydrochloric and sulphuric acids, with evolution of hydrogen gas; in dilute nitric acid, with evolution of nitrous oxide; in more concentrated nitric acid, with evolution of nitric oxide.

2. The OXIDE OF ZINC and its HYDRATE are white powders, which are insoluble in water, but dissolve readily in hydrochloric, nitric, and sulphuric acids. The oxide of zinc acquires a lemon-yellow tint when heated, but it reassumes its original white color upon cooling. When ignited before the blowpipe, it shines with considerable brilliancy.

3. The SALTS OF OXIDE OF ZINC are colorless; part of them are soluble in water, the rest in acids. The neutral salts of zinc which are soluble in water redden litmus-paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which can bear a dull red heat, without undergoing decomposition. Chloride of zinc is volatile at a red heat.

4. *Hydrosulphuric acid* precipitates from neutral solutions of salts of zinc a portion of the metal as white hydrated SULPHIDE OF ZINC (Zn S). In acid solutions this reagent fails altogether to produce a precipitate if the free acid present is one of the stronger acids; but from a solution of oxide of zinc in acetic acid, it throws down the whole of the zinc, even if the acid is present in excess. [Solutions of zinc, containing a free, strong acid, are partially, or even completely precipitated when *very largely diluted with water.* —*Eliot* and *Storer.*]

5. *Sulphide of ammonium* throws down from *neutral*, and *hydrosulphuric acid* from *alkaline* solutions of salts of zinc, the whole of the metal as hydrated SULPHIDE OF ZINC, in form of a white precipitate. Chloride of ammonium promotes the separation of this precipitate. From very dilute solutions it deposits only after long standing. This precipitate is not redissolved by an excess of sulphide of ammonium, nor by potassa or ammonia; but it dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid. It is insoluble in acetic acid.

6. *Potassa and soda* throw down from solutions of salts of zinc

HYDRATED OXIDE OF ZINC (Zn O, H O), in form of a white, gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. Upon boiling these alkaline solutions they remain, if concentrated, unaltered; but from dilute solutions nearly the whole of the oxide of zinc separates as a white precipitate. Chloride of ammonium does not precipitate alkaline solutions of oxide of zinc.

7. *Ammonia* also produces in solutions of oxide of zinc, if they do not contain a large excess of free acid, a precipitate of HYDRATED OXIDE OF ZINC, which readily dissolves in an excess of the precipitant. The concentrated solution turns turbid when mixed with water. On boiling the concentrated solution, part of the oxide of zinc separates immediately; on boiling the dilute solution, all the oxide of zinc precipitates.

8. *Carbonate of soda* produces in solutions of salts of zinc a precipitate of BASIC CARBONATE OF ZINC (3 [Zn O, H O]+2 [Zn O, C O_2]+4 aq.), which is insoluble in an excess of the precipitant. Presence of salts of ammonia in great excess prevents the formation of this precipitate.

9. *Carbonate of ammonia* also produces in solutions of salts of zinc the same precipitate of BASIC CARBONATE OF ZINC as carbonate of soda; but this precipitate redissolves upon further addition of the precipitant. On boiling the dilute solution, oxide of zinc precipitates.

10. *Carbonate of baryta* fails to precipitate solutions of oxide of zinc in the cold, solution of the sulphate excepted.

11. If a mixture of oxide of zinc, or one of its salts, with *carbonate of soda* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a slight coating of OXIDE OF ZINC, which presents a yellow color whilst hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame.

12. If oxide of zinc or one of the salts of zinc is moistened with solution of *nitrate of protoxide of cobalt*, and then heated before the blowpipe, an unfused mass is obtained, of a beautiful GREEN color: this mass is a compound of oxide of zinc with protoxide of cobalt. If, therefore, in the experiment described in 11 the charcoal is moistened, around the little cavity, with solution of nitrate of protoxide of cobalt, the coating appears *green* when *cold*.

§ 110.

b. PROTOXIDE OF MANGANESE (Mn O).

1. METALLIC MANGANESE is whitish-gray in color, extremely hard, eminently susceptible of polish, brittle, and fuses with very great difficulty. Exposed to the air it shortly tarnishes, on heating it at

first acquires a colored tarnish like steel, afterwards becomes coated with brown oxide. It oxidizes slowly in cold water, rapidly in boiling water, and dissolves readily in acids. The solutions contain protoxide.

2. PROTOXIDE OF MANGANESE is grayish-green; the hydrated protoxide is white. Both the protoxide and its hydrate absorb oxygen from the air, and are converted into the brown sesquioxide. They are readily soluble in hydrochloric, nitric, and sulphuric acids.

1. The HIGHER OXIDES OF MANGANESE all dissolve in hot hydrochloric acid to protochloride, at the same time evolving chlorine. On heating with concentrated sulphuric acid they give off oxygen and yield protosulphate of Manganese.

2. The SALTS OF PROTOXIDE OF MANGANESE are colorless or pale red; part of them are soluble in water, the rest in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colors.

4. *Hydrosulphuric acid* does not precipitate acid solutions of salts of protoxide of manganese; neutral solutions also it fails to precipitate, or precipitates them only very imperfectly.

5. *Sulphide of ammonium* throws down from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of manganese, the whole of the metal as hydrated SULPHIDE OF MANGANESE (Mn S), in form of a light flesh-colored* precipitate, which acquires a dark-brown color in the air; this precipitate is insoluble in sulphide of ammonium and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids. From very dilute solutions the precipitate separates only after standing some time in a warm place. Solutions containing much free ammonia should be nearly neutralized with hydrochloric acid. The separation of the precipitate is facilitated by chloride of ammonium.

6. *Potassa*, *soda*, and *ammonia* produce whitish precipitates of HYDRATE OF PROTOXIDE OF MANGANESE (Mn O, H O), which upon exposure to the air speedily acquire a brownish and finally a deep blackish-brown color, owing to the conversion of the hydrated protoxide into hydrated sesquioxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate; but presence of chloride of ammonium prevents the precipitation by ammonia altogether, and that by potassa partly. Of *already-formed* precipitates, solution of chloride of ammonium redissolves only those parts, which have not yet undergone peroxidation. The solution of the hydrated protoxide of manganese in chloride of ammonium is owing to the disposition of

* If the quantity of the precipitate is only trifling, the color appears yellowish-white.

the salts of protoxide of manganese to form double salts with salts of ammonia. The ammoniacal solutions of the double salts turn brown in the air, and deposit dark-brown hydrate of sesquioxide of manganese.

7. If a few drops of a fluid containing protoxide of manganese, and free from chlorine, are sprinkled on *binoxide of lead*, or *red-lead*, nitric acid free from chlorine added, the mixture boiled and allowed to settle, the fluid is of a PURPLE RED color from the formation of nitrate of sesquioxide of manganese, [according to *Rose*,— of permanganic acid, according to *Crum*, and *Hoppe-Seyler*.]

8. *Carbonate of baryta* does not precipitate protoxide of manganese from its solutions, upon digestion in the cold, solution of sulphate of manganese excepted.

9. If any compound of manganese, in a state of minute division, is fused with *carbonate of soda* on a platinum wire in the *outer* flame of the blowpipe, or gas-lamp, MANGANATE OF SODA ($Na\ O$, $Mn\ O_3$) is formed, which makes the fused mass appear GREEN while hot, and of a BLUISH-GREEN tint after cooling, the bead at the same time becoming turbid. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test may be still further increased by the addition of a minute quantity of nitrate of potassa to the carbonate of soda. [If the compound is not soluble in carbonate of soda, a little borax should be added.]

10. *Borax* and *phosphate of soda and ammonia* dissolve manganese compounds in the *outer* flame of the blowpipe to clear VIOLET-RED beads, which upon cooling acquire an AMETHYST-RED tint: they lose their color in the *inner* flame, owing to a reduction of the sesquioxide to protoxide. The bead which borax forms with manganese compounds, appears black when containing a considerable portion of sesquioxide of manganese, but that formed by phosphate of soda and ammonia never loses its transparency. But the latter loses its color in the inner flame of the blowpipe far more readily than the former.

§ 111.

c. PROTOXIDE OF NICKEL ($Ni\ O$).

1. METALLIC NICKEL in the fused state is silvery white, inclining to gray; it is bright, hard, malleable, ductile, difficultly fusible; it does not oxidize in the air at common temperatures, but it oxidizes slowly upon ignition; it is attracted by the magnet, and may itself become magnetic. It slowly dissolves in hydrochloric acid and dilute sulphuric acid upon the application of heat, the solution being attended with evolution of hydrogen gas. It dissolves readily in nitric acid. The solutions contain protoxide of nickel.

2. HYDRATED PROTOXIDE OF NICKEL is green and inalterable in

the air. By ignition it is converted into grayish-green PROTOXIDE. Both are easily soluble in hydrochloric, nitric, and sulphuric acids. The octahedrally crystallized protoxide of nickel is, however, insoluble in acids though soluble in fused bisulphate of potash. SESQUIOXIDE OF NICKEL is black and soluble in hydrochloric acid with evolution of chlorine, forming protochloride of nickel.

3. Most of the SALTS OF PROTOXIDE OF NICKEL are yellow in the anhydrous, green in the hydrated state; their solutions are of a light green color. The soluble neutral salts slightly redden litmus-paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* does not precipitate solutions of salts of nickel which contain one of the stronger acids in the free state. In absence of free acid these solutions gradually yield a slight precipitate of black SULPHIDE OF NICKEL (Ni S). Acetate of nickel, containing excess of acetic acid, is not at all, or but slightly precipitated; in absence of free acid the larger part of the nickel is thrown down by prolonged action of the reagent.

5. *Sulphide of ammonium* produces in neutral, and *hydrosulphuric acid* in alkaline solutions of salts of ~~protoxide of nickel~~, a black precipitate of hydrated SULPHIDE OF NICKEL (Ni S), which is not altogether insoluble in sulphide of ammonium, especially if containing free ammonia; the fluid from which the precipitate has been thrown down exhibits therefore usually a brownish color. Chloride of ammonium greatly promotes the precipitation. Sulphide of nickel dissolves scarcely at all in acetic acid, with great difficulty in hydrochloric acid, but readily in nitrohydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce a light green precipitate of HYDRATE OF PROTOXIDE OF NICKEL (Ni O, H O), which is insoluble in an excess of the precipitants, and unalterable in the air. Carbonate of ammonia dissolves this precipitate, when filtered and washed, to a greenish-blue fluid, from which potassa or soda reprecipitates the nickel as an apple-green hydrate of protoxide of nickel.

7. *Ammonid* added in small quantity to solutions of protoxide of nickel produces in them a trifling greenish turbidity; upon further addition of the reagent this redissolves readily to a blue fluid containing a compound of protoxide of nickel and ammonia. Potassa and soda precipitate from this solution hydrate of protoxide of nickel. Solutions containing salts of ammonia or free acid are not rendered turbid by ammonia.

8. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL (Ni Cy), which redissolves readily in an excess of the precipitant as a double cyanide of nickel and potassium (Ni Cy + K Cy); the solution is brownish-yellow. If sulphuric acid or hydrochloric acid is added to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel reprecipi-

tated; the latter substance is very difficultly soluble in an excess of these acids in the cold, but more readily upon boiling.

9. *Carbonate of baryta* does not precipitate protoxide of nickel from its solutions, upon digestion in the cold solution of sulphate of nickel excepted.

10. *Nitrite of potassa*, used in conjunction with acetic acid, fails to precipitate even concentrated solutions of nickel.

11. *Borax* and *phosphate of soda and ammonia* dissolve compounds of protoxide of nickel in the *outer* flame to clear beads; the bead produced with borax is violet whilst hot, reddish-brown when cold; the bead produced with the phosphate of soda and ammonia is reddish, inclining to brown whilst hot, but turns yellow or reddish-yellow upon cooling. The bead which phosphate of soda and ammonia forms with salts of protoxide of nickel remains unaltered in the *inner* flame of the blowpipe, but that formed with borax turns gray and turbid from reduced metallic nickel. Upon continued exposure to the blowpipe flame the particles of nickel unite, but without fusing to a grain, and the bead becomes colorless.

§ 112.

d. Protoxide of Cobalt (Co O).

1. Metallic cobalt in the fused state is steel-gray, pretty hard, susceptible of polish, malleable, difficultly fusible, and magnetic; it oxidizes very slowly in the air at the common temperature, more rapidly at a red heat; with acids it comports itself like nickel. The solutions contain protoxide of cobalt.

2. Protoxide of cobalt is an olive-green, its hydrate a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids. The sesquioxide of cobalt ($Co_2 O_3$) is black, and dissolves in hydrochloric acid to protochloride of cobalt, with evolution of chlorine.

3. The salts of protoxide of cobalt, containing water of crystallization, are red, the anhydrous salts mostly blue. The moderately concentrated solutions appear of a light red color, which they retain even though considerably diluted. The soluble neutral salts redden litmus-paper slightly, and are decomposed at a red heat; sulphate of protoxide of cobalt alone can bear a moderate red heat without suffering decomposition. When a solution of chloride of cobalt is evaporated, the light red color changes towards the end of the operation to blue; addition of water restores the red color.

4. *Hydrosulphuric acid* does not precipitate solutions of cobalt, which contain one of the stronger acids in the free state. In absence of free acid there gradually separates from these solutions a portion of the cobalt, as black sulphide (Co S). Acetate of

cobalt containing free acid is scarcely or not at all precipitated; in absence of free acid, all or nearly all the cobalt is thrown down.

5. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of protoxide of cobalt, the whole of the metal as black hydrated SULPHIDE OF COBALT (Co S). Chloride of ammonium greatly favors its separation. This substance is insoluble in alkalies and sulphide of ammonium, scarcely soluble in acetic acid, very difficultly in hydrochloric acid, but readily so in nitrohydrochloric acid upon application of heat.

6. *Potassa* and *soda* produce in solutions of cobalt BLUE precipitates of basic salts of cobalt, which turn GREEN upon exposure to the air, owing to the absorption of oxygen; upon boiling, they are converted into pale red hydrate of protoxide of cobalt, which contains alkali, and generally appears rather discolored from an admixture of sesquioxide formed in the process. These precipitates are insoluble in solutions of potassa and soda; but neutral carbonate of ammonia dissolves them completely to intensely violet-red fluids, in which a somewhat larger proportion of potassa or soda produces a blue precipitate, the fluid still retaining its violet color.

7. *Ammonia* produces the same precipitate as potassa, but this redissolves in an excess of the ammonia to a reddish-brown fluid, from which solution of potassa or soda throws down part of the cobalt as a blue basic salt. Ammonia fails to precipitate solutions of protoxide of cobalt containing salts of ammonia or free acid.

8. Addition of *cyanide of potassium* to a solution of cobalt gives rise to the formation of a brownish-white precipitate of PROTOCYANIDE OF COBALT (Co Cy), which dissolves readily as a double cyanide of cobalt and potassium in an excess of solution of cyanide of potassium. Acids precipitate from this solution cyanide of cobalt. But if the solution is boiled with cyanide of potassium in excess, in presence of free hydrocyanic acid (liberated by addition of one or two drops of hydrochloric acid), a double compound of sesquicyanide of cobalt and cyanide of potassium (cobalticyanide of potassium, $K_3, Co_2\ Cy_6 = K_3\ Ckdy$) is formed, in the solution of which acids *produce no precipitate* (important distinction from nickel).

9. *Carbonate of baryta* does not precipitate solutions of protoxide of cobalt in the cold, sulphate of cobalt excepted.

10. If *nitrite of potassa* is added in not too small proportion to a solution of protoxide of cobalt, then acetic acid to *strongly* acid reaction, and the mixture put in a moderately warm place, all the cobalt separates, from concentrated solutions immediately or very soon, from dilute solutions after some time, as NITRITE OF SESQUI-

OXIDE OF COBALT AND POTASSA ($Co_2 O_3$, 3 K O, 5 N O_3, 2 H O), in form of a crystalline precipitate of a beautiful yellow color. The mode in which this precipitate forms may be seen from the following equation: 2 (Co O, S O_3) + 6 (K O, N O_3) + $\bar{A}$ = K O, $\bar{A}$ + 2 (K O, S O_3) + $Co_2 O_3$, 3 K O, 5 N O_3 + N O_2. The precipitate is only sparingly soluble in pure water, and altogether insoluble in saline solutions and in alcohol. When boiled with water, it dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down hydrate of protoxide of cobalt (*Fischer, Aug. Stromeyer*). This excellent reaction enables us to distinguish nickel from cobalt. It is always necessary to concentrate the solution of protoxide of cobalt to a considerable extent before adding the nitrite of potassa.

11. *Borax* dissolves compounds of cobalt both in the *inner* and *outer* flame of the blowpipe, giving clear beads of a magnificent BLUE color, which appear violet by candle-light, and almost black if the cobalt is present in considerable proportion. This test is as delicate as it is characteristic. *Phosphate of soda and ammonia* manifests with salts of cobalt before the blowpipe an analogous but less delicate reaction.

§ 113.

e. PROTOXIDE OF IRON (Fe O).

1. METALLIC IRON in the pure state has a light whitish-gray color (iron containing carbon is more or less gray); the metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture a coating of rust (hydrate of sesquioxide of iron) forms on its surface; upon ignition in the air, a coating of black protosesquioxide. Hydrochloric acid and dilute sulphuric acid dissolve iron, with evolution of hydrogen gas; if the iron contains carbon, the hydrogen is mixed with carbide of hydrogen. The solutions contain protoxide. Dilute nitric acid dissolves iron in the cold to nitrate of protoxide, with evolution of nitrous oxide; at a high temperature, to nitrate of sesquioxide, with evolution of nitric oxide; if the iron contains carbon, some carbonic acid is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies, or in some cases, graphite remains.

2. PROTOXIDE OF IRON is a black powder; its HYDRATE is a white powder, which in the moist state absorbs oxygen and speedily acquires a grayish-green, and ultimately a brownish-red color. Both the protoxide and its hydrates are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. The SALTS OF PROTOXIDE OF IRON have in the anhydrous state a white, in the hydrated state a greenish color; their solu-

tions appear colored only when concentrated. Exposed to the air, they absorb oxygen and are converted into salts of the protosesquioxide with separation of basic sesquisalts. The soluble neutral salts redden litmus-paper, and are decomposed at a red heat.

4. Acid solutions of salts of protoxide of iron are not precipitated by *hydrosulphuric acid;* neutral solutions of salts of protoxide of iron with weak acids are precipitated by this reagent at the most but very incompletely; the precipitates are of a black color.

5. *Sulphide of ammonium* precipitates from neutral, and hydrosulphuric acid from alkaline solutions of salts of protoxide of iron, the whole of the metal as black hydrated PROTOSULPHIDE OF IRON (Fe S), which is insoluble in alkalies and sulphides of the alkali metals, but dissolves readily in hydrochloric and nitric acids: this black precipitate turns reddish-brown in the air by oxidation. To highly dilute solutions of protoxide of iron, addition of sulphide of ammonium imparts a green color, and it is only after some time that the protosulphide of iron separates as a black precipitate. Chloride of ammonium greatly facilitates the precipitation.

6. *Potassa* and *ammonia* produce a precipitate of HYDRATE OF PROTOXIDE OF IRON (Fe O, H O), which in the first moment looks almost white, but acquires after a very short time a dirty green, and ultimately a reddish-brown color, owing to absorption of oxygen from the air. Presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If alkaline solutions of protoxide of iron thus obtained by the agency of salts of ammonia are exposed to the air, hydrates of protosesquioxide and of sesquioxide of iron precipitate.

7. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON (K, Fe_3, Cfy_2), which, by absorption of oxygen from the air, speedily acquires a blue color. Nitric acid or chlorine converts it immediately into Prussian blue, 3 (K, Fe_3, Cfy_2) + 4 Cl = 3 K Cl + Fe Cl + 2 (Fe_1 Cfy_3).

8. *Ferricyanide of potassium* produces a magnificently blue precipitate of FERRICYANIDE OF IRON (Fe_3 Cfdy). This precipitate does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions of salts of protoxide of iron the reagent produces simply a deep blue-green coloration.

9. *Sulphocyanide of potassium* does not alter solutions of protoxide of iron free from sesquioxide.

10. *Carbonate of Baryta* does not precipitate solutions of protoxide of iron in the cold, solution of the sulphate excepted.

11. *Borax* dissolves salts of protoxide of iron in the *oxidizing* flame, giving beads varying in color from YELLOW to DARK-RED; when cold, the beads vary from colorless to dark-yellow. In the

inner flame the beads change to bottle-green, owing to the reduction of the newly-formed sesquioxide to protosesquioxide. *Phosphate of soda and ammonia* manifests a similar deportment with the salts of protoxide of iron; the beads produced with this reagent lose their color upon cooling still more completely than is the case with those produced with borax; the signs of the ensuing reduction in the reducing flame are also less marked.

§ 114.

f. Sesquioxide of Iron ($Fe_2 O_3$).

1. The native crystallized SESQUIOXIDE OF IRON is steel-gray; the native as well as the artificially prepared sesquioxide of iron gives upon trituration a brownish-red powder; the color of hydrate of sesquioxide of iron is more inclined to reddish-brown. Both the sesquioxide and its hydrate dissolve in hydrochloric, nitric, and sulphuric acids; the hydrate dissolves readily in these acids, but the anhydrous sesquioxide dissolves with greater difficulty, and completely only after long exposure to heat. The PROTOSESQUIOXIDE (magnetic oxide Fe O, $Fe_2 O_3$) is black, and dissolves in hydrochloric acid to a mixture of proto- and sesquichloride, in aqua regia to sesquichloride of iron.

2. The neutral anhydrous SALTS OF SESQUIOXIDE OF IRON are nearly white; the basic salts are yellow or reddish-brown. The color of the solutions is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble neutral salts redden litmus-paper, and are decomposed by heat.

3. *Hydrosulphuric acid* produces in acid solutions of salts of sesquioxide of iron containing the stronger acids, a milky white turbidity, proceeding from separated SULPHUR. At the same time the sesquisalt is converted into a protosalt. $Fe_2 O_3, 3 S O_3 + H S = 2 (Fe O, S O_3) + H O, S O_3 + S$. Solution of hydrosulphuric acid, rapidly added to neutral solutions, imparts to the fluid a transitory blackening. In solution of neutral acetate of sesquioxide of iron it precipitates the greater part of the iron. In presence of a sufficient quantity of free acetic acid only sulphur separates.

4. *Sulphide of ammonium* precipitates from neutral, and *hydrosulphuric acid* from alkaline solutions of salts of sesquioxide of iron, the whole of the metal as black hydrated PROTOSULPHIDE OF IRON (Fe S) mixed with sulphur. This precipitation is preceded by the reduction of the sesquioxide to protoxide. $Fe_2 Cl_3 + 3 N H_4 S = 3 N H_4 Cl + 2 Fe S + S$. In very dilute solutions the reagent produces only a blackish-green coloration. The minutely divided protosulphide of iron subsides in such cases only after long standing. Its separation is greatly favored by presence of chloride of ammonium. Protosulphide of iron, as already stated (§113.5.), is

insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric and nitric acids.

5. *Potassa* and *ammonia* produce bulky reddish-brown precipitates of HYDRATE OF SESQUIOXIDE OF IRON ($Fe_2 O_3, 3H O$), which are insoluble in an excess of the precipitant as well as in salts of ammonia.

6. *Ferrocyanide of potassium* produces even in highly dilute solutions a magnificently blue precipitate of FERROCYANIDE OF IRON, or Prussian blue ($Fe_4 Cfy_3$): $2 (Fe_2 Cl_3) + 3 (Cfy. 2 K) = 6 K Cl + Fe_4 Cfy_3$. This precipitate is insoluble in hydrochloric acid, but is decomposed by potassa, with separation of hydrate of sesquioxide of iron.

7. *Ferricyanide of potassium* deepens the color of solutions of salts of sesquioxide of iron to reddish-brown; but it fails to produce a precipitate.

8. *Sulphocyanide of potassium* imparts to neutral or slightly acid solutions of salts of sesquioxide of iron a most intense blood-red color, arising from the formation of a soluble SULPHOCYANIDE OF IRON.* Addition of acetate of soda† destroys this color, hydrochloric acid restores it again. This test is the most delicate of all; it will indicate the presence of sesquioxide of iron even in fluids which are so highly dilute that every other reagent fails to produce the slightest visible alteration. The red coloration may in such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top.

[9. When a solution containing a sesquisalt of iron is rendered nearly neutral by carbonate of soda, and then heated to boiling with addition of excess of *acetate of soda*, all the iron is precipitated as brown BASIC SESQUIACETATE, and may be completely removed from the solution by filtering hot and washing with boiling water. If it is allowed to remain in the solution it partially redissolves as the latter becomes cold.]

10. *Carbonate of baryta* precipitates even in the cold all the iron as a basic salt mixed with hydrate of sesquioxide.

11. The reactions before the *blowpipe* are the same as with the protoxide.

§ 115.

Recapitulation and remarks.—On observing the behavior of the oxides of the fourth group with solution of soda, it would appear that the separation of the oxide of zinc, which is soluble in

[* A similar coloration is produced by sulphocyanide of potassium in solutions containing binoxide of molybdenum or hyponitric acid.]

[† So also phosphates, borates, fluorides, oxalates, tartrates, racemates, malates, citrates, succinates, and the corresponding acids.]

an excess of this reagent, might be readily effected by its means; however, in the actual experiment, we find that in the presence of sesquioxide of iron, protoxide of cobalt, &c., some of the oxide of zinc precipitates with these oxides; and if only a small quantity of oxide of zinc is present, it frequently occurs that no trace of this metal can be detected in the alkaline filtrate. This method would be entirely worthless in case sesquioxide of chromium were present, because oxide of zinc and sesquioxide of chromium mutually precipitate each other from their alkaline solutions.

Again, from the behavior of the different oxides with chloride of ammonium and an excess of ammonia, one would conclude that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also applied to the mixed oxides, is inaccurate, since greater or smaller portions of the other oxides will always precipitate with the sesquioxide of iron; and it may therefore happen that, in this process, small quantities of cobalt, manganese, &c., altogether escape detection.

It is far safer therefore to separate the other oxides of the fourth group from sesquioxide of iron by carbonate of baryta (with addition of chloride of ammonium), as in that case the iron is precipitated free from oxide of zinc and protoxide of manganese, and mixed only with a very trifling quantity of protoxides of nickel and cobalt.

Protoxide of manganese may conveniently be separated from the protoxides of cobalt and nickel and from oxide of zinc, by treating the precipitated and washed sulphides with moderately dilute acetic acid, which dissolves the sulphide of manganese, leaving the other sulphides unacted on. If the acetic acid solution is now mixed with solution of soda, the least trace of a precipitate will be sufficient to recognize the manganese before the blowpipe with carbonate of soda.

If the sulphides left undissolved by acetic acid, after being washed are treated with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the fluid is then boiled and considerably concentrated, to expel the hydrosulphuric acid, and afterwards treated cold with solution of potassa or soda in excess, the zinc is sure to be detected in the filtrate by hydrosulphuric acid.

If the filter which may contain the sulphides of nickel and cobalt is dried and burned in a small porcelain dish, and a portion of the residue tested with borax in the inner blowpipe flame, cobalt is usually recognized without difficulty [or in its absence, nickel is at once detected]. The detection of nickel in presence of cobalt is not so easy. It succeeds best by the following method. To the concentrated solution, nitrite of potassa is added in considerable

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quantity, then acetic acid to strongly acid reaction, and the mixture is finally set aside in a moderately warm place for at least 12 hours. All the cobalt will thus separate as nitrite of cobalt and potassa. It is then filtered, the nickel in the filtrate is precipitated with caustic soda, and tested before the blowpipe.

Since in the course of analysis the oxides of the fourth group are usually thrown down together by sulphide of ammonium as sulphides, it is most convenient to separate the nickel and cobalt, or at least, all but traces of these metals at the outset. For this purpose, the precipitated sulphides while still moist are agitated with water and some hydrochloric acid in the cold. Sulphides of nickel and cobalt remain almost entirely undissolved, while the sulphides of all the other metals of the fourth group at once go into solution. The sulphides of nickel and cobalt are filtered off, washed, and treated as above directed. The filtrate is boiled with addition of some nitric acid, whereby the iron is converted into sesquioxide. The free acid is now nearly neutralized with carbonate of soda and the sesquioxide of iron is precipitated either in the cold by addition of carbonate of baryta, or by boiling with acetate of soda and filtering hot. The filtrate contains finally manganese and zinc. These are again thrown down with sulphide of ammonium, chloride of ammonium being likewise added, filtered off, washed and separated as above described with acetic acid, or this solution is freed from baryta by addition of excess of sulphuric acid and filtration; the filtrate is reduced to a small bulk by evaporation, and treated with soda-solution, which throws down manganese and retains zinc in solution. The small quantities of nickel and cobalt which might have passed into solution in the first treatment of the precipitated sulphides with hydrochloric acid, remain with the sulphide of zinc when this is separated from sulphide of manganese by acetic acid; or in case oxide of zinc was separated by soda-solution from oxide of manganese, they are found with the latter. In the former instance sulphide of zinc may be extracted from the blackish precipitate by dilute hydrochloric acid. In the latter case manganese may be at once detected by means of carbonate of soda, in the outer blowpipe flame, even in presence of nickel and cobalt.

Protoxide and sesquioxide of iron may be detected in presence of each other, by testing for the former with ferricyanide of potassium, for the latter with ferrocyanide of potassium, or, better still, with sulphocyanide of potassium.*

In conclusion, it is necessary to mention that alkalies fail to precipitate the oxides of the fourth group, and carbonate of baryta does not throw down sesquioxide of iron, in presence of non-volatile

* [Compare Molybdenum, § 138. b.]

organic substances (such as sugar, tartaric acid, &c.) We have already seen that the same applies to alumina.

Special Reactions of the rarer Oxides of the Fourth Group.

§ 116.

1. OXIDES OF URANIUM. Uranium is of comparatively rare occurrence in pitch-blende, uranium-ochre, &c. Its sesquioxide is employed in making yellow-green glass. It forms two oxides, the protoxide (U O) and the sesquioxide ($U_2 O_3$). The first is brown and dissolves in nitric acid to nitrate of sesquioxide. Hydrated sesquioxide is yellow; at about 570° Fah. loses its water and becomes red; on ignition it is converted into the dark blackish-green protosesquioxide. The solutions of sesquioxide of uranium in acids are yellow. They are not altered by *hydrosulphuric acid*. *Sulphide of ammonium* throws down, after neutralization of the free acid, a slowly subsiding precipitate, whose color varies from dirty yellow to red-brown, and is sometimes even blood-red, according to the presence and relative quantities of chloride of ammonium, ammonia, and sulphide of ammonium. Chloride of ammonium facilitates its separation. The precipitate is readily soluble in acids, even in acetic acid; it is insoluble in sulphide of ammonium. It is not pure sulphide of uranium, but contains, besides uranium and sulphur, ammonium, oxygen, and water. *Ammonia*, *potassa*, and *soda* produce yellow precipitates of sesquioxide of uranium and alkali, insoluble in excess of the precipitants. *Carbonate of ammonia*, and the *bicarbonates of soda and potassa*, produce yellow precipitates of carbonate of sesquioxide of uranium and alkali, which *dissolve readily in an excess of the precipitant*. Potassa and soda throw down from these solutions the whole of the sesquioxide of uranium. *Carbonate of baryta* completely precipitates solutions of sesquioxide of uranium, even in the cold. *Ferrocyanide of potassium* produces a reddish-brown precipitate; this is a very delicate test for uranium. *Borax* and *phosphate of soda and ammonia* give with sesquioxide of uranium in the inner flame of the blowpipe green beads, in the outer flame yellow beads, which upon cooling acquire a yellowish-green tint.

2. OXIDES OF VANADIUM. Vanadium is met with but very rarely in the form of salts of vanadic acid, sometimes it exists in minute quantity in iron and copper ores and in the slags which result from their smelting. Vanadium has three oxides, viz.: suboxide (V O), binoxide ($V O_2$), and vanadic acid ($V O_5$). The lower oxides of vanadium are converted into vanadic acid by heating with nitric or nitrohydrochloric acids, and by fusion with nitrate of potassa. Vanadic acid is yellowish-red, fusible at an incipient red heat, not volatile, and becomes crystalline on solidification. It is very slightly soluble in water, but reddens litmus-paper strongly. It unites both with acids and bases.

a. Acid solutions. Vanadic acid dissolves in the stronger acids, forming yellow or red liquids. The solutions are often decolorized by boiling. Sulphurous acid, many metals, organic matters, &c., color the solutions blue by reducing vanadic acid to binoxide of vanadium. *Hydrosulphuric acid* does not precipitate acidified solutions, but colors them blue, sulphur separating. *Sulphide of ammonium* colors the solutions brown, and by acidifying with hydrochloric, or better with sulphuric acid, brown tersulphide of vanadium separates, which is soluble in excess of sulphide of ammonium, giving a red-brown liquid. *Ferrocyanide of potassium* throws down a green precipitate. *Tincture of galls*, after some time, gives a blue-black precipitate.

b. Vanadates. The neutral salts are mostly yellow. The salts of the alkalies and some others, when warmed with water, become colorless. The acid salts are yellowish-red. The salts withstand a red heat; they are mostly soluble in water, and are all dissolved by nitric acid. The alkaline vanadates are the less soluble in water the more free alkali or alkaline salt is present. On saturating the solution

of an alkaline vanadate with *chloride of ammonium* all the vanadic acid is thrown down as a white vanadate of ammonia, which is insoluble in excess of the precipitant (especially characteristic reaction). This precipitate, when ignited, yields vanadate of binoxide of vanadium.—On agitating the acidified solution of an alkaline vanadate with *binoxide of hydrogen*, the solution acquires a red color, the liquid remains red even after shaking with ether, the latter being unchanged (very delicate reaction).—(*Werther.*) *Borax* dissolves vanadic acid to a clear bead, which in the outer flame is colorless, or with large quantities yellow: in the inner flame green, or with large quantities brownish while hot, and green on cooling.

[3. OXIDES OF THALLIUM. Thallium occurs in minute quantities in many native metallic sulphides, especially in iron and copper pyrites. Hence it is often found in commercial sulphur, in oil of vitriol, and in the sediment of sulphuric acid chambers, in metallic copper, bismuth, and cadmium, and in preparations derived from these substances; also in certain mineral springs, and in the flue-dust of furnaces. Thallium is a bluish-white, very soft and malleable, though not tenacious metal. Its sp. gr.=11.8: it is brilliant on a fresh surface, but shortly tarnishes. It is easily fusible and volatilizes at a red heat, and before the blowpipe emits copious fumes of oxide which have a peculiar odor and exhibit white, reddish, and violet colors. It dissolves readily in sulphuric and nitric acids, with difficulty in hydrochloric acid. Boiled with hydrochloric acid or aqua regia, chloride of thallium escapes in the vapors. It dissolves slowly as oxide in distilled water, especially when in a state of fine division. —Of the compounds of oxygen with thallium there are known a protoxide, a sesquioxide, and a teroxide. Protoxide of thallium as hydrate, is largely soluble in water and alcohol; its solution reddens litmus, is caustic and alkaline; by evaporation *in vacuo* it is obtained crystallized in the form of yellow needles. It absorbs carbonic acid with avidity, unites with acids yielding crystallizable salts.—*Hydrosulphuric acid* does not affect acid solutions of thallium, but throws down from alkaline, as *sulphide of ammonium* does from neutral and alkaline solutions, all the thallium they contain as brownish-black (according to Böttger grayish-black) sulphide in form of a *very bulky* flocculent precipitate, which becomes less voluminous on heating or agitation. Sulphide of thallium is insoluble in sulphide of ammonium, in alkalies, alkaline carbonates and cyanides. It oxidizes to soluble sulphate on exposure to the air, and must hence be washed with dilute sulphide of ammonium. It is slowly but perceptibly soluble in cold dilute acetic, hydrochloric and sulphuric acids, especially if exposed to the air, as happens when treated on a filter with these acids. It dissolves readily in nitric acid.

According to Böttger there exists a higher sulphide of thallium, which has a red color. It is obtained mixed with sulphur, by cautious addition of *hyposulphite of soda* to the boiling acid solutions of thallium. It also appears to be formed to some extent when the solutions of thallium are treated with sulphide of ammonium, a yellow, brownish-yellow or red-brown coloration appearing in cold dilute solutions, and on heating, the liquid assumes a purplish or blue color by transmitted, and is yellow or brownish-red by reflected light, while, after standing, a brownish precipitate separates, which, treated with dilute acids, leaves a slowly soluble or insoluble red residue. This sulphide is inalterable in the air.—*Alkalies* and *alkaline carbonates* produce no precipitates in solutions of thallium. *Hydrochloric acid* throws down from solutions that are not too dilute, protochloride of thallium as a white, curdy, quickly subsiding precipitate, which requires 50 parts of boiling water and 200 parts of cold water for its solution, and is less soluble in water containing hydrochloric acid. It is but slightly soluble in ammonia or in alcohol. *Chromate of potassa* gives yellow, and *bichromate of potassa* deep orange precipitates, which are nearly insoluble in water and acids. *Phosphate of soda* gives a crystalline precipitate soluble in acids, but almost insoluble in water and alkaline liquids.

Iodide of potassium, a very sensitive reagent, gives a pale yellow precipitate of

iodide of thallium, which appears to be but slightly soluble either in water or excess of the reagent.

Bichloride of platinum throws down a pale orange precipitate of platinchloride of thallium, which is next to the sulphide, the least soluble salt of thallium yet described

Metallic zinc separates all the thallium in the metallic state, from neutral solutions often in form of brilliant, radiated, needle shaped crystals, from acid solutions as a heavy black powder.

Thallium and its compounds are most easily and certainly detected by spectral analysis. The *spectrum* is characterized by a single bright green line coincident with Ba, δ, as seen in Plate I. It is, however, usually perceptible for but a moment, and its intensity and duration do not safely indicate the amount of thallium present in sulphides, flue-dust, &c.

To find thallium in native sulphur the latter is mostly dissolved by sulphide of carbon, and the residue examined as above. In pyrites, flue dust and sulphuric acid-chamber sediment, it may be usually detected at once by the spectroscope. The sublimate obtained by strongly heating finely pulverized sulphides in a closed glass tube often gives the reaction when none can be obtained from the substance itself.]

§ 117.

FIFTH GROUP.

Of Common Occurrence: Oxide of Silver, Suboxide of Mercury, Oxide of Mercury, Oxide of Lead, Teroxide of Bismuth, Oxide of Copper, Oxide of Cadmium.

Of Rare Occurrence: Oxides of Palladium, Rhodium, Osmium and Ruthenium.

Properties of the group.—The sulphides corresponding to the oxides of this group are insoluble both in dilute acids and in alkaline sulphides.* The solutions of these oxides are therefore completely precipitated by hydrosulphuric acid, no matter whether their reaction be neutral, alkaline, or acid.

The circumstance that they are thrown down by hydrosulphuric acid from *acid solutions* distinguishes the oxides of the fifth group from those of the fourth, and all the former groups.

For the sake of greater clearness and simplicity, we divide the oxides of this group into two divisions, and distinguish,

1. Oxides precipitable by hydrochloric acid, viz.: oxide of silver, suboxide of mercury, oxide of lead.

2. Oxides not precipitable by hydrochloric acid, viz.: oxide of mercury, oxide of copper, teroxide of bismuth, oxide of cadmium.

Lead must be considered in both divisions, since the sparing solubility of its chloride might lead to confounding its oxide with suboxide of mercury and oxide of silver, without affording us, on the other hand, any means of effecting its perfect separation from the oxides of the second division.

* Consult, however, the paragraphs on oxide of copper and suboxide and oxide of mercury, as the latter remark applies only partially to them.

Special Reactions of the more commonly occurring oxides.

FIRST DIVISION: OXIDES WHICH ARE PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

§ 118

a. OXIDE OF SILVER (Ag O).

1. METALLIC SILVER is white, very lustrous, moderately hard, highly malleable, ductile, rather difficultly fusible. It is scarcely oxidized by ignition in the air. Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. OXIDE OF SILVER is a grayish-brown powder; it is not altogether insoluble in water, and dissolves readily in dilute nitric acid. It forms no hydrate. It is decomposed by heat into metallic silver and oxygen gas. The SUBOXIDE OF SILVER (Ag_2 O) and the BINOXIDE (Ag O_2) suffer the same decomposition by ignition.

3. The SALTS OF OXIDE OF SILVER are non-volatile and colorless; most of them acquire a black tint upon exposure to light. The soluble neutral salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* precipitate from solutions of salts of silver black SULPHIDE OF SILVER (Ag S), which is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassa* and *soda* precipitate from solutions of salts of silver the oxide of this metal in the form of a LIGHT BROWN POWDER, which is insoluble in an excess of the precipitant, but dissolves readily in ammonia.

6. *Ammonia*, when added in very small quantity to neutral solutions of oxide of silver, throws down the *oxide* as a brown precipitate, which readily redissolves in an excess of ammonia. Acid solutions of silver are not precipitated.

7. *Hydrochloric acid* and *soluble metallic chlorides* produce in solutions of salts of silver a white, curdy precipitate of CHLORIDE OF SILVER (Ag Cl). In very dilute solutions these reagents impart at first simply a bluish-white opalescent appearance to the fluid; by long standing, however, the chloride of silver separates. By the action of light, chloride of silver is slowly decomposed, losing chlorine, and acquiring at first a violet tint, but ultimately turning black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound the chloride of silver is again separated by acids. Concentrated hydro-

chloric acid and concentrated solutions of chlorides of the alkali metals dissolve some chloride of silver, more particularly upon application of heat; but the dissolved chloride separates again upon dilution. Upon exposure to heat, chloride of silver fuses without decomposition, giving upon cooling a transparent horny mass.

8. If compounds of silver, mixed with *carbonate of soda*, are exposed on a charcoal support to the *inner* flame of the blowpipe, WHITE, BRILLIANT, DUCTILE METALLIC GLOBULES are obtained, unattended with incrustation of the charcoal; or, if the blast be intense and prolonged, with the formation of a slight dark-red sublimate.

§ 119.

b. SUBOXIDE OF MERCURY (Hg_2O).

1. METALLIC MERCURY is grayish-white, lustrous, fluid at the common temperature; it solidifies at —40°, and boils at 680° Fah. It is insoluble in hydrochloric acid; in dilute cold nitric acid it dissolves to nitrate of suboxide, in more concentrated hot nitric acid to nitrate of oxide of mercury.

2. SUBOXIDE OF MERCURY is a black powder which is readily soluble in nitric acid, and is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

3. The SALTS OF SUBOXIDE OF MERCURY volatilize upon ignition; most of them suffer decomposition in this process. Subchloride and subbromide of mercury volatilize unaltered. Most of the salts of suboxide of mercury are colorless. The soluble salts in the neutral state redden litmus paper. Nitrate of suboxide of mercury is decomposed by addition of much water into a pale-yellow, insoluble basic, and a soluble acid salt.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce black precipitates of SUBSULPHIDE OF MERCURY (Hg_2S), which are insoluble in dilute acids, sulphide of ammonium, and cyanide of potassium. Protosulphide of sodium in presence of some caustic soda dissolves this subsulphide to sulphide, with separation of metallic mercury. Bisulphide of sodium dissolves the subsulphide to sulphide, without separation of metallic mercury. Subsulphide of mercury is readily decomposed and dissolved by nitrohydrochloric acid, but not by boiling concentrated nitric acids.

5. *Soda*, *potassa* and *ammonia* produce in solutions of salts of suboxide of mercury black precipitates, which are insoluble in an excess of the precipitants. The precipitates produced by soda and potassa consist of SUBOXIDE OF MERCURY; whilst those produced by ammonia consist of a BASIC DOUBLE SALT OF SUBOXIDE OF MERCURY AND AMMONIA, *e. g.* ($N H_3$, $N O_5$ + 2 Hg_2O).

6. *Hydrochloric acid* and *soluble chlorides* precipitate from solutions of salts of suboxide of mercury SUBCHLORIDE OF MERCURY

(Hg_2 Cl) as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid fail to dissolve this precipitate; it dissolves, however, although very difficultly and slowly, upon long protracted boiling with these acids, being resolved by hydrochloric acid into chloride of mercury and metallic mercury, which separates; and converted by nitric acid into chloride of mercury and nitrate of oxide of mercury. Nitrohydrochloric acid and chlorine water dissolve the subchloride of mercury readily, converting it into chloride. Ammonia and potassa decompose the subchloride of mercury, the first gives rise to the formation of amido-subchloride of mercury, (Hg_2 N H_2, Hg_2 Cl) the latter separates black suboxide from it.

7. If a drop of a neutral or slightly acid solution of suboxide of mercury is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards, on being gently rubbed with cloth, paper, &c., appear WHITE and LUSTROUS like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the apparent silvering.

8. *Protochloride of tin* produces in solutions of suboxide of mercury a gray precipitate of METALLIC MERCURY, which may be united into globules by boiling the metallic deposit, after decanting the fluid, with hydrochloric acid, to which a drop of protochloride of tin may be added.

9. If an intimate mixture of an anhydrous compound of mercury with anhydrous *carbonate of soda* is introduced into a drawn-out glass tube, and covered with a layer of carbonate of soda, and the tube is then heated before the blowpipe, the mercurial compound invariably undergoes decomposition, and metallic mercury separates, forming a coat of gray sublimate above the heated part of the tube. The minute particles of mercury may be united into larger globules by rubbing this coating with a glass rod.

§ 120.

c. OXIDE OF LEAD (Pb O).

1. METALLIC LEAD is bluish-gray; its surface recently cut exhibits a metallic lustre; it is soft, malleable, readily fusible, and volatile at a white heat. Fused upon charcoal before the blowpipe, it forms a coating of yellow oxide on the charcoal. Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat; but dilute nitric acid dissolves it readily, more particularly on heating.

2. OXIDE OF LEAD is a yellow or reddish-yellow powder,* which

* While hot, the oxide of lead appears red.

upon exposure to a red heat fuses to a vitreous mass. Hydrated oxide of lead is white. Both the oxide and its hydrate dissolve readily in nitric and acetic acids. The SUBOXIDE OF LEAD ($Pb_2 O$) is black, MINIUM or red-lead ($2 Pb O, Pb O_2$) is red, the BINOXIDE $Pb O_2$ is brown. These are all converted by ignition into oxide. The binoxide is insoluble in hot nitric acid, but dissolves on addition of alcohol, yielding nitrate of oxide of lead.

8. The SALTS OF OXIDE OF LEAD are non-volatile; most of them are colorless; the neutral soluble salts redden litmus paper, and are decomposed at a red heat. Chloride of lead when heated with access of air, partially volatilizes and oxychloride of lead remains behind.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in solutions of salts of lead black precipitates of SULPHIDE OF LEAD (Pb S), which are insoluble in *cold* dilute acids, in alkalies, alkaline sulphides, and cyanide of potassium. Sulphide of lead is decomposed by boiling nitric acid. If the acid be sufficiently dilute the whole of the lead dissolves as nitrate of lead, and sulphur separates. Fuming nitric acid oxidizes the sulphur entirely to sulphuric acid, and all the lead separates as insoluble sulphate of lead. Nitric acid of medium strength causes the separation of a portion of the lead as sulphate, while the remainder remains in the form of nitrate. In solutions of salts of lead containing an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water or after neutralization of the free acid by an alkali. If a solution of lead is precipitated by hydrosulphuric acid, in presence of a large quantity of free hydrochloric acid, a red precipitate may be formed, consisting of chloride and sulphide of lead, which, however, is converted by an excess of hydrosulphuric acid into black sulphide of lead.

5. *Soda*, *potassa* and *ammonia* throw down BASIC SALTS OF LEAD in the form of white precipitates, which are insoluble in ammonia, and difficultly soluble in soda and potassa. In solutions of acetate of lead ammonia (free from carbonate,) does not immediately produce a precipitate, owing to the formation of a soluble triacetate of lead.

6. *Carbonate of soda* throws down from solutions of salts of lead a white precipitate of BASIC CARBONATE OF LEAD (*e. g.* 6 (Pb O, C O_2) + Pb O, H O), which is insoluble in an excess of the precipitant and also in cyanide of potassium.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions of salts of lead heavy, white precipitates of CHLORIDE OF LEAD (Pb Cl), which are soluble in a large amount of water, especially upon application of heat. This chloride of lead is converted by ammonia into oxychloride of lead (Pb Cl, 3 Pb O + H O), which is also a white powder, but almost absolutely

insoluble in water. In dilute nitric and hydrochloric acids, chloride of lead is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce in solutions of salts of lead white precipitates of SULPHATE OF LEAD (Pb O, S O_3), which are nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the sulphate of lead precipitates only after some, frequently after a long time. It is advisable under all circumstances to add a considerable *excess* of dilute sulphuric acid, since sulphate of lead is more insoluble in this menstruum than in water. The separation of small quantities of sulphate of lead is best effected by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa. It dissolves also pretty readily in the solutions of some of the salts of ammonia, particularly in solution of acetate of ammonia; dilute sulphuric acid precipitates it again from these solutions.

9. *Chromate of potassa* produces in solutions of salts of lead a yellow precipitate of CHROMATE OF LEAD (Pb O, Cr O_3) which is readily soluble in potassa, but difficultly so in dilute nitric acid.

10. If a mixture of a compound of lead with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blow-pipe*, soft, malleable METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a slight yellow incrustation of OXIDE OF LEAD.

§ 121.

Recapitulation and remarks.—The metallic oxides of the first division of the fifth group are most distinctly characterized in their corresponding chlorides; since the different respective deportment of these chlorides with water and ammonia affords us a simple means both of detecting them and effecting their separation from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the chloride of lead dissolves, whilst the chloride of silver and the subchloride of mercury remain undissolved. If these two chlorides are then treated with ammonia, the subchloride of mercury is converted into a black basic salt, insoluble in an excess of the ammonia; whilst the chloride of silver dissolves readily in that agent, and precipitates from this solution again upon addition of nitric acid. When operating upon small quantities, it is advisable first to expel the greater part of the ammonia by heat. In the aqueous solution

of chloride of lead the metal may be readily detected by sulphuric acid.

SECOND DIVISION OF THE FIFTH GROUP: OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

§ 122.

a. Oxide of Mercury (Hg O.)

1. Oxide of Mercury is generally crystalline, and has a bright red color, which upon reduction to powder changes to a pale yellowish-red; the oxide precipitated from solutions of the nitrate of the oxide, or from solutions of the chloride, forms a yellow powder. Upon exposure to heat it transiently acquires a deeper tint; at a dull red heat it is resolved into metallic mercury and oxygen. Both the crystalline and non-crystalline oxide dissolve readily in hydrochloric and nitric acids.

2. The salts of oxide of mercury volatilize upon ignition; most of them suffer decomposition in this process; chloride, bromide, and iodide of mercury, however, volatilize unaltered. Most of the salts of oxide of mercury are colorless. The soluble neutral salts redden litmus paper. The nitrate and sulphate of oxide of mercury are decomposed by water added in large quantity, into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrosulphuric acid* or *sulphide of ammonium* produces in solutions of oxide of mercury, after shaking, a perfectly white precipitate. Addition of a somewhat larger quantity of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color, according to the less or greater proportion added; an excess of the precipitant produces a purely black precipitate of sulphide of mercury (Hg S). This progressive variation of color from white to black, which depends on the proportion of the hydrosulphuric acid or sulphide of ammonium added, distinguishes the oxide of mercury from all other bodies. The white precipitate which forms at first consists of a double compound of sulphide of mercury with the still undecomposed portion of the salt of oxide of mercury (in a solution of chloride of mercury, for instance, Hg Cl + 2 Hg S); the gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of color above mentioned. Sulphide of mercury is not dissolved by sulphide of ammonium, nor by potassa or cyanide of potassium; it is altogether insoluble in hydrochloric acid and in nitric acid, even upon boiling. It dissolves completely in sulphide of potassium, and is readily decomposed and dissolved by nitrohydrochloric acid.

4. *Soda* or *potassa*, added in small quantity, produces in neutral or slightly acid solutions of oxide of mercury a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The *reddish-brown* precipitate is a BASIC SALT; the *yellow* precipitate consists of OXIDE OF MERCURY. An excess of the precipitant does not redissolve these precipitates. In very acid solutions this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of salts of ammonia, potassa produces in solutions of salts of oxide of mercury, instead of reddish-brown or yellow, *white* precipitates. The precipitate thrown down by potassa from a solution of chloride of mercury containing an excess of chloride of ammonium is of analogous composition to the precipitate produced by ammonia (see 5).

5. *Ammonia* produces in solutions of salts of oxide of mercury white precipitates quite analogous to those produced by potassa in presence of chloride of ammonium; thus, for instance, ammonia precipitates from solutions of chloride of mercury, CHLORAMIDE OF MERCURY ($Hg\,Cl + Hg\,N\,H_2$).

6. *Protochloride of tin*, added in small quantity to salts of oxide of mercury, reduces the oxide to suboxide, thus giving rise to the formation of a white precipitate of SUBCHLORIDE OF MERCURY ($2\,Hg\,Cl + Sn\,Cl = Hg_2\,Cl + Sn\,Cl_2$); but if added in excess, the subchloride at first formed is reduced to METAL ($Hg_2\,Cl + Sn\,Cl = Sn\,Cl_2 + Hg_2$). The precipitate, which was white at first, acquires therefore now a gray tint, and may be readily united into globules of metallic mercury by boiling with hydrochloric acid, and some protochloride of tin.

7. The salts of oxide of mercury present the same deportment as the salts of the suboxide, both with metallic *copper* and when heated together with *carbonate of soda* in a glass tube before the blowpipe.

§ 123.

b. OXIDE OF COPPER (Cu O).

1. METALLIC COPPER has a peculiar red color, and a strong lustre; it is moderately hard, malleable, ductile, rather difficultly fusible; in contact with water and air it becomes covered with a green crust of basic carbonate of oxide of copper; upon ignition in the air it becomes coated over with black oxide. In hydrochloric acid and dilute sulphuric acid it is insoluble or nearly so, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into sulphate of oxide of copper, with evolution of sulphurous acid.

2. SUBOXIDE OF COPPER is red, its hydrate yellow; both change to oxide upon ignition in the air. On treating the suboxide with dilute sulphuric acid, metallic copper separates, whilst sulphate of

oxide of copper dissolves; on treating suboxide of copper with hydrochloric acid, white subchloride of copper is formed, which dissolves in an excess of the acid, but is reprecipitated from this solution by water.

3. OXIDE OF COPPER is a black powder; its hydrate (Cu O, H O) is of a light blue color. Both the oxide of copper and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids.

4. Most of the neutral SALTS OF OXIDE OF COPPER are soluble in water; the soluble salts redden litmus, and suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; the hydrated salts are usually of a blue, or green color, which their solutions continue to exhibit even when much diluted.

5. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of oxide of copper, brownish-black precipitates of SULPHIDE OF COPPER (Cu S). This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of sulphide of potassium and sulphide of sodium fail also to dissolve it, or dissolve it only to a very trifling extent; but it is a little more soluble in sulphide of ammonium. [Sulphide of ammonium may produce in the cold a red-brown or red precipitate which dissolves completely in an excess of the reagent, but is perfectly or almost perfectly precipitated as black sulphide when the solution is heated to boiling.] The latter reagent is therefore not adapted to effect the perfect separation of sulphide of copper from other metallic sulphides. Sulphide of copper is readily decomposed and dissolved by boiling concentrated nitric acid; it dissolves completely in solution of cyanide of potassium. In solutions of salts of copper which contain an excess of a concentrated mineral acid, hydrosulphuric acid produces a precipitate only after the addition of water.

6. *Potassa* or *soda* produces in solutions of salts of oxide of copper a light blue, bulky precipitate of HYDRATE OF OXIDE OF COPPER (Cu O, H O). If the solution is highly concentrated, and the potassa added in excess, the precipitate turns black after the lapse of some time, and loses its bulkiness, even in the cold; but the change takes place immediately if the precipitate is boiled with the fluid in which it is suspended (and which must, if necessary, be diluted for the purpose). In this process Cu O, H O, is converted into 3 Cu O, H O.

7. *Carbonate of soda* produces in solutions of salts of oxide of copper a greenish-blue precipitate of HYDRATED BASIC CARBONATE OF COPPER ($Cu O, C O_2 + Cu O, H O$), which upon boiling changes to brownish-black oxide of copper, and dissolves in ammonia to an azure-blue, and in cyanide of potassium to a brownish fluid.

8. *Ammonia* added in small quantity to solutions of salts of oxide of copper produces a greenish-blue precipitate, consisting of a BASIC SALT OF COPPER. This precipitate redissolves readily upon further addition of ammonia, giving a perfectly clear solution of a magnificent azure-blue, which owes its color to the formation of a BASIC DOUBLE SALT OF AMMONIO-OXIDE OF COPPER. Thus, for instance, in a solution of sulphate of oxide of copper, ammonia produces a precipitate of $N H_3$, Cu O + $N H_4$ O, S O_3. The blue color ceases to be perceptible only in very dilute solutions. Potassa produces in such blue solutions in the cold, after the lapse of some time, a precipitate of blue hydrate of oxide of copper; but upon boiling the fluid this reagent precipitates the whole of the copper as black oxide. Carbonate of ammonia presents the same deportment with salts of copper as pure ammonia.

9. *Ferrocyanide of potassium* produces even in moderately dilute solutions a reddish-brown precipitate of FERROCYANIDE OF COPPER (Cu_2, Cfy) which is insoluble in dilute acids, but suffers decomposition when acted upon by potassa or ammonia. In very highly dilute solutions the reagent produces only a reddish coloration of the fluid.

10. *Metallic iron* when brought into contact with concentrated solutions of salts of copper is almost immediately covered with a COPPERY-RED COATING OF METALLIC COPPER; very dilute solutions produce this coating only after some time. Presence of a little free acid accelerates the reaction.

If a fluid containing copper and a little free hydrochloric acid is poured into a small *platinum dish* (the lid of a platinum crucible), and a small piece of *zinc* is introduced, the bright platinum surface speedily becomes covered with a COATING OF COPPER; even with *very* dilute solutions this coating is clearly discernible.

11. If a mixture of a compound of copper with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, METALLIC COPPER is obtained, without simultaneous incrustation of the charcoal. The best method of freeing this copper from the particles of charcoal, is to triturate the fused mass in a small mortar with water, and to wash off the charcoal powder; when the coppery-red metallic particles will be left behind.

12. Copper, its alloys, and other compounds, when exposed in even the minutest quantities to the *inner blowpipe or gas-flame*, impart an EMERALD GREEN tint to the outer flame. Addition of hydrochloric acid considerably heightens the delicacy of the reaction.

13. *Borax* and *phosphate of soda* and *ammonia* readily dissolve oxide of copper in the outer flame. The beads are green while hot, blue when cold. In the inner flame the bead produced with borax appears colorless, that produced with phosphate of soda and

ammonia turns dark green; both acquire a brownish-red tint upon cooling.

§ 124.

c. TEROXIDE OF BISMUTH ($Bi O_3$).

1. BISMUTH has a reddish tin-white color and moderate metallic lustre; it is of medium hardness, brittle, readily fusible; when fused upon a charcoal support, it forms a coating of yellow teroxide on the surface of the charcoal. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid, and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into sulphate of teroxide of bismuth, with evolution of sulphurous acid.

2. The TEROXIDE OF BISMUTH is a yellow powder; when heated, it transiently acquires a deeper tint; it fuses at a red heat. Hydrate of teroxide of bismuth is white. Both the teroxide and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids. Grayish-black BINOXIDE OF BISMUTH ($Bi O_2$) and red BISMUTHIC ACID ($Bi O_5$) are converted into teroxide by ignition in the air, and yield with hot nitric acid, nitrate of teroxide.

3. The SALTS OF TEROXIDE OF BISMUTH are non-volatile, with the exception of a few (terchloride of bismuth). Most of them are soluble in water, whilst others are insoluble in this menstruum. The soluble salts, in the neutral state, redden litmus-paper, and are decomposed when treated with a large amount of water, insoluble basic salts separating, the greater portion of the acid and a small quantity of bismuth remaining however in solution.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in neutral and acid solutions of salts of bismuth black precipitates of TERSULPHIDE OF BISMUTH ($Bi S_3$), which are insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium, but are readily decomposed and dissolved by boiling nitric acid. In solutions of salts of bismuth which contain a considerable excess of hydrochloric or nitric acid, hydrosulphuric acid produces a precipitate only after the addition of water.

5. *Potassa* and *ammonia* throw down from solutions of salts of bismuth HYDRATE OF TEROXIDE OF BISMUTH as a white precipitate, which is insoluble in an excess of the precipitant.

6. *Carbonate of soda* throws down from solutions of salts of bismuth BASIC CARBONATE OF BISMUTH ($Bi O_3, C O_2$) as a white bulky precipitate, which is insoluble in an excess of the precipitant, and equally so in cyanide of potassium.

7. *Chromate of potassa* precipitates from solutions of salts of bismuth CHROMATE OF BISMUTH ($Bi O_3, 2 Cr O_3$) as a yellow powder. This substance differs from chromate of lead in being soluble in dilute nitric acid and insoluble in potassa.

8. *Dilute sulphuric acid* does not precipitate dilute solutions of nitrate of bismuth. If the solution containing excess of sulphuric acid be evaporated to dryness in the water-bath, there remains a white saline mass, which dissolves perfectly in water acidified with sulphuric acid (characteristic distinction from oxide of lead). From this solution, after long standing (perhaps for days), basic sulphate of bismuth ($Bi_2 S O_3 + 2$ aq.) crystallizes out in white microscopic needles which are soluble in nitric acid.

9. The reaction which especially characterizes the teroxide of bismuth, is the decomposition of its neutral salts by *water* with the formation of insoluble basic salts. The addition of a large amount of water to solutions of salts of bismuth, causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. This reaction is the most sensitive with terchloride of bismuth, as the basic OXYCHLORIDE OF BISMUTH ($Bi Cl, 2 Bi_2 O_3$) is nearly insoluble in water. If water fails to produce a precipitate in nitric acid solutions of bismuth, owing to the presence of too much free acid, adding solution of chloride of sodium nearly always causes an immediate precipitation. From the basic salts of antimony which are formed under analogous circumstances, the precipitated basic salts of bismuth may be readily distinguished by their insolubility in tartaric acid.

10. If a mixture of a compound of bismuth with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight incrustation of TEROXIDE OF BISMUTH, which is orange when hot, and yellow when cold.

§ 125.

d. OXIDE OF CADMIUM (Cd O).

1. METALLIC CADMIUM has a tin-white color; it is lustrous, not very hard, malleable, ductile; it fuses at a temperature below red heat, and volatilizes at a temperature somewhat above the boiling point of mercury. It may therefore be easily sublimed in a glass tube. Heated on charcoal before the blowpipe, it takes fire and burns, emitting brown fumes of oxide of cadmium, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen; but nitric acid dissolves it most readily.

2. OXIDE OF CADMIUM is a yellowish-brown, fixed powder; its hydrate is white. Both the oxide and its hydrate dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The SALTS OF OXIDE OF CADMIUM are colorless or white; some of them are soluble in water. The soluble salts, in the neutral state, redden litmus-paper, and are decomposed at a red heat.

4. *Hydrosulphuric acid* and *sulphide of ammonium* produce in alkaline, neutral, and acid solutions of salts of cadmium, bright yellow precipitates of SULPHIDE OF CADMIUM (Cd S), which are insoluble in dilute acids, alkalies, alkaline sulphides, and (distinction from copper) in cyanide of potassium. They are readily decomposed and dissolved by boiling nitric and hydrochloric acids, and (distinction from copper) in boiling dilute sulphuric acid. In solutions of salts of cadmium which contain a considerable excess of acid, hydrosulphuric acid produces a precipitate only after dilution with water.

5. *Potassa* produces in solutions of salts of cadmium a white precipitate of HYDRATE OF OXIDE OF CADMIUM (Cd O, H O), which is insoluble in an excess of the precipitant.

6. *Ammonia* likewise precipitates from solutions of salts of cadmium white HYDRATE OF OXIDE OF CADMIUM, which, however, redissolves readily to a colorless fluid in an excess of the precipitant.

7. *Carbonate of potassa* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM (Cd O, C O_2), which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates. The precipitated carbonate of cadmium dissolves readily in solution of cyanide of potassium. From dilute solutions the precipitate separates only after some time.

8. If a mixture of a compound of cadmium with *carbonate of soda* is exposed on a charcoal support to the *reducing flame of the blowpipe*, the charcoal becomes covered with a reddish-brown coating of OXIDE OF CADMIUM, owing to the volatilization of the reduced metal and its subsequent re-oxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

§ 126.

Recapitulation and remarks.—The perfect separation of the metallic oxides of the second division of the fifth group from suboxide of mercury and oxide of silver may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. Traces of salts of oxide of mercury which may adhere to the chloride of silver are completely dissolved by washing.—(*G. J. Mulder.*) The oxide of mercury is distinguished from the other oxides of this division by the insolubility of the corresponding sulphide in boiling nitric acid. This property affords a convenient means for its separation. Care must be taken that the sulphides be *completely* freed from hydrochloric acid and metallic chlorides before treating them with nitric acid, as otherwise, mercury would go into solution. Moreover, the reactions with protochloride of tin or with metallic copper, as

well as those in the dry way, will, after the previous removal of the suboxide, always readily indicate the presence of oxide of mercury.

If the humid method be employed, it is best to dissolve the sulphide of mercury in hot hydrochloric acid with help of a fragment of chlorate of potassa.

From the still remaining oxides the oxide of lead is separated by addition of a sufficient quantity of dilute sulphuric acid; the separation is the most complete if the fluid, after the addition of sulphuric acid, is evaporated on the water-bath, the residue diluted with water containing some sulphuric acid and the insoluble sulphate of lead immediately filtered off. The latter can be examined in the dry way as described, § 120.10, or by heating a portion of it with solution of chromate of potassa. The white precipitate is thus converted into the yellow chromate of lead. It is washed and heated with soda-solution in which it dissolves. Addition of acetic acid to the alkaline solution throws down again yellow chromate of lead. After removal of the oxides of mercury and lead, teroxide of bismuth may be separated from oxide of copper and oxide of cadmium by addition of ammonia in excess, as the latter two oxides are soluble in an excess of this agent. If the filtered precipitate is dissolved in one or two drops of hydrochloric acid on a watchglass, and water added, the appearance of a milky turbidity is a confirmation of the presence of teroxide of bismuth.—The presence of a notable quantity of oxide of copper is revealed by the blue color of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then ferrocyanide of potassium. The separation of copper from cadmium may be effected by acting on the mixed sulphides of these metals by cyanide of potassium, or by boiling dilute sulphuric acid. The solution of the two metals is precipitated by hydrosulphuric acid and the sulphides are filtered off. If the sulphides be now covered with water and a fragment of cyanide of potassium added, the sulphide of copper dissolves, while yellow sulphide of cadmium remains behind. If the mixed sulphides be boiled with dilute sulphuric acid (1 part of strong acid to 6 parts of water) sulphide of cadmium is dissolved while sulphide of copper is unattacked. From the solution hydrosulphuric acid throws down yellow sulphide of cadmium.—(*A. W. Hoffman.*)

Special reactions of the rarer oxides of the fifth group.

§ 127.

1. Protoxide of Palladium (Pd O).—Palladium greatly resembles platinum, with which it is usually associated in nature. Its color is, however, somewhat darker. It fuses with great difficulty; when heated in the air to dull redness, it becomes covered with a blue coating; but, upon more intense ignition, it recovers its light color and metallic lustre. It is difficultly soluble in pure nitric acid, but dissolves

somewhat more readily in nitric acid, containing nitrous acid; it dissolves very sparingly in boiling concentrated sulphuric acid, but readily in nitro-hydrochloric acid. It combines with 1 and 2 eq. of oxygen to form protoxide and binoxide. The latter in black, and when heated with dilute hydrochloric acid, evolves chlorine, and gives solution of protochloride of palladium. Protoxide of palladium is black, its hydrate dark brown; both are, upon intense ignition, resolved into oxygen and metallic palladium. The salts of protoxide of palladium are mostly soluble in water; they are brown, or reddish-brown; their solutions, when concentrated, are reddish-brown; when dilute, yellow. Water precipitates from a solution of nitrate of protoxide of palladium containing a slight excess of acid, a brown-colored basic salt. The oxygen salts, as well as the protochloride, are decomposed upon ignition, leaving metallic palladium behind. *Hydrosulphuric acid* and *sulphide of ammonium* throw down from acid or neutral solutions of salts of protoxide of palladium, black protosulphide of palladium, which dissolves neither in sulphide of ammonium nor in boiling hydrochloric acid, and with difficulty in boiling nitric acid, but readily in nitro-hydrochloric acid. From the solution of the protochloride *potassa* precipitates a brown basic salt, soluble in an excess of the precipitant, *ammonia*, flesh-colored *ammonio-protochloride of palladium* (Pd Cl, N H_3), *cyanide of mercury*, yellowish-white gelatinous *protocyanide of palladium* soluble in hydrochloric acid, and in ammonia (characteristic reaction). *Protochloride of tin* produces, in absence of free hydrochloric acid, a brownish-black precipitate; in presence of free hydrochloric acid, a red-colored solution, which speedily turns brown, and ultimately green, and, upon addition of water, brownish-red. *Sulphate of protoxide of iron* produces a deposit of palladium on the sides of the glass. *Iodide of potassium* precipitates black protiodide of palladium (characteristic reaction). *Chloride of potassium* precipitates from highly concentrated solutions of protoxide of palladium, potassio-protochloride of palladium (K Cl, Pd Cl), in form of golden-yellow needles, which dissolve readily in water, giving a dark red fluid, but are insoluble in absolute alcohol.

2. Sesquioxide of Rhodium.—(R_2 O_3). Rhodium is found in small quantity in native platinum. It is a steel-gray, hard, brittle metal. In the state of powder it acquires oxygen at a red heat, and passes first into protoxide, afterwards into protosesquioxide. On stronger ignition it is reduced again to the metallic state. Rhodium is insoluble in all acids, even in nitro-hydrochloric. It dissolves in the latter when it is alloyed with platinum, copper, &c., but not when alloyed with gold and silver. It is dissolved as sesquioxide by fused hydrated phosphoric acid, as well as bisulphate of potassa. The sesquioxide is black, its hydrate greenish gray, or brown; it is insoluble in acids, but soluble in the fluxes above named. The solutions are rose red. *Hydrosulphuric acid* and *sulphide of ammonium* slowly precipitate, especially from warm solutions, brown sulphide of rhodium, which is insoluble in sulphide of ammonium but dissolves in boiling hydrochloric and nitric acids. *Potassa* precipitates brown hydrate only on boiling. If alcohol be added to the solution, made alkaline by potassa, rhodium is thrown down in the form of a black powder. The precipitation takes place only after the lapse of some time, when potassa is present in large excess.

Ammonia produces, after some time, a yellow precipitate which is soluble in hydrochloric acid. *Zinc* throws down black metallic rhodium. All the solid compounds of rhodium, when ignited in a stream of hydrogen, yield the metal, which is well characterized by its insolubility in nitrohydrochloric acid, its solubility in fusing bisulphate of potassa and the deportment of the solution towards potassa and alcohol.

3. Oxides of Osmium.—Osmium accompanies native platinum as Iridosmine, &c. It is either a black powder or a gray brilliant mass, and is infusible. The metal, as well as its protoxide (O O) and binoxide (Os O_2), oxidize easily when heated in the air, to *osmic acid* (Os O_4) which is volatile and recognizable by its highly character-

istic, penetrating, and disagreeable odor, resembling that of chlorine and iodine. If osmium be placed on a strip of platinum foil, and brought into the outer mantel of the *gas* or *alcohol flame* at half its height, the flame becomes intensely luminous. In iridium containing minute traces of osmium, the latter may thus be detected; the reaction is, however, momentary; it may be reproduced by bringing the substance for a time into the reducing flame and then again into the outer mantel. *Nitric acid*, especially when red and fuming, and nitrohydrochloric acid, dissolve osmium to osmic acid. The solution is favored by heat, but with loss of osmic acid. Osmium which has been intensely ignited does not dissolve in acids. It should be fused with nitrate of potassa and the fused mass distilled with nitric acid; osmic acid passes into the distillate.

When osmium is heated in *chlorine*, there are formed green volatile protochloride of osmium (Os Cl), and red, still more volatile bichloride (Os Cl_2). The bichloride of osmium in solution rapidly decomposes, unless an alkaline chloride be present, into hydrochloric acid, osmic acid, and metallic osmium. All compounds of osmium yield, when heated in *hydrogen* gas, metallic osmium. Anhydrous osmic acid is white and crystalline, fusible at a gentle heat, boils at about 212° Fah., giving off vapors that attack the eyes and nostrils. Heated with water, it fuses and dissolves but slowly. The solution has a faint acid reaction and a strong disagreeable odor. Its solution is colored yellow, and its odor disappears on addition of *alkalies*. On heating with nitric or hydrochloric acid, the odor is again developed, and on distilling the mixture, osmic acid passes over (highly characteristic reaction). On evaporating solutions of alkaline osmates, especially if alkali be in excess, osmous acid (Os O_2) is formed. The reduction is aided by addition of alcohol. *Hydrosulphuric acid* produces brown sulphide of osmium (Os S_4), which only separates in presence of a strong acid; it is insoluble in sulphide of ammonium. *Sulphite of soda* gives a deep blue-violet color, and osmium gradually separates as a black powder. Osmium is also thrown down as a black powder by *protosulphate of iron* and by *formic acid*, and in presence of a strong acid, by zinc and many other metals. The osmochloride of potassium is difficultly soluble in cold, more easily in hot water; it is insoluble in alcohol. On heating its solution with *tannic acid* it becomes of a deep blue color (characteristic); *formate of soda* throws down from it black metallic osmium.

4. OXIDES OF RUTHENIUM.—Ruthenium is found in small quantities in native platinum. It is a gray-white, brittle, very infusible metal, not attacked by fusing bisulphate of potassa, scarcely by aqua-regia; ignited in the air, it is converted into bluish-black sesquioxide ($Ru_2 O_3$) which is insoluble in acids; ignited in a stream of chlorine gas with chloride of potassium, it gives ruthenochloride of potassium; fused with hydrate, nitrate or chlorate of potassa it yields a greenish-black mass containing ruthenate of potassa (Ko Ru O_3), which dissolves in water to an orange-yellow solution, that colors the skin black, from reduction and separation of black sesquioxide. From this solution, acids precipitate black oxide which is dissolved by hydrochloric acid, to an orange-yellow liquid. The latter solution is decomposed by heating, into hydrochloric acid and brownish-black oxide of ruthenium; it gives when concentrated, crystalline, violet, shining precipitates with chlorides of ammonium and potassium, from which on boiling, black oxyprotochloride separates. *Potassa* throws down black hydrated oxide of ruthenium, which is insoluble in alkalies and soluble in acids. *Hydrosulphuric acid* at first, produces no change. After some time the solution becomes sky-blue, and brown sulphide of ruthenium separates (very characteristic reaction). *Sulphide of ammonium* gives a brown-black precipitate, which slightly dissolves in excess of the precipitant. *Sulphocyanide of potassium* produces (in absence of the other platinum metals), and after some time, a red coloration which gradually becomes purple, and on heating, violet (very characteristic reaction). *Zinc* causes at first a sky-blue coloration, and afterwards a decoloration of the liquid with separation of metallic ruthenium.

§ 128.

SIXTH GROUP.

Of common occurrence: TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE OF ANTIMONY, ARSENIOUS ACID AND ARSENIC ACID.

Of rare occurrence: OXIDES OF IRIDIUM, MOLYBDENUM, TUNGSTEN, TELLURIUM AND SELENIUM.

The higher oxides of the elements belonging to the sixth group all possess more or less marked acid characters; they are however noticed here because they cannot be conveniently considered apart from the lower oxides of the same elements, especially as they deport themselves similarly towards hydrosulphuric acid.

Properties of the group.—The sulphides corresponding to the oxides of the sixth group are insoluble in dilute acids. These combine with alkaline sulphides either directly, or by passing into a higher degree of sulphuration, forming soluble sulphur salts, in which they perform the part of the acid. Hydrosulphuric acid precipitates these oxides therefore, like those of the fifth group, completely from acidified solutions. The precipitated sulphides differ, however, from those of the fifth group in this, that they dissolve in sulphide of ammonium, sulphide of potassium, &c., and are reprecipitated from these solutions on the addition of acids.

We divide the oxides of this group into two classes, and distinguish,

1. OXIDES WHOSE CORRESPONDING SULPHIDES ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, and are reduced to the metallic state upon fusion in conjunction with nitrate and carbonate of soda: viz., teroxide of gold and binoxide of platinum.

2. OXIDES WHOSE CORRESPONDING SULPHIDES ARE SOLUBLE IN BOILING HYDROCHLORIC ACID OR NITRIC ACID, and are upon fusion with nitrate and carbonate of soda converted into oxides or acids, which combine with the soda: viz., Teroxide of antimony, protoxide and binoxide of tin, arsenious and arsenic acids.

FIRST DIVISION.

Special Reactions.

§ 129.

a. TEROXIDE OF GOLD ($Au O_3$).

1. METALLIC GOLD has a reddish yellow color, and a high metallic lustre: it is rather soft, exceedingly malleable, ductile, difficultly fusible: it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids; but it dissolves in fluids containing or evolving chlorine, *e. g.* in nitro-hydrochloric acid. The solution contains terchloride of gold.

2. TEROXIDE OF GOLD is a blackish-brown, its hydrate a chesnut-brown powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little teroxide of gold; water reprecipitates it from these solutions. The protoxide of gold (Au O) in violet-black, on heating it is resolved into gold and oxygen.

3. SALTS OF GOLD with oxygen acids are nearly unknown. The haloid salts of gold are yellow, and their solutions continue to exhibit this color up to a high degree of dilution. The whole of them are readily decomposed upon ignition. Neutral solution of terchloride of gold reddens litmus-paper.

4. *Hydrosulphuric acid* precipitates from neutral and acid solutions of gold the whole of the metal in the cold, as brown black TERSULPHIDE OF GOLD (Au S_3), when hot, as PROTOSULPHIDE OF GOLD (Au S). These precipitates are insoluble in nitric or hydrochloric acid; but dissolve in aqua regia. They are insoluble in colorless sulphide of ammonium, but dissolve in the yellow alkaline sulphides, especially in yellow sulphides of potassium and sodium.

5. *Sulphide of ammonium* throws down TERSULPHIDE OF GOLD. This redissolves in an excess of the precipitant only if the latter contains an excess of sulphur.

6. *Ammonia* produces, but only in tolerably concentrated solutions of gold, reddish-yellow precipitates of AURATE OF AMMONIA (fulminating gold). The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Protochloride of tin* containing an admixture of bichloride (procured by adding a little chlorine water to protochloride), produces even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of PURPLE OF CASSIUS, is insoluble in hydrochloric acid. It is assumed to be a hydrated compound of binoxide of tin and protoxide of gold with protoxide and binoxide of tin (Au O, $Sn O_2$ + Sn O, $Sn O_2$ + 4 H O).

8. *Salts of protoxide of iron* reduce the teroxide of gold, when added to its solutions, and precipitate metallic gold in form of a most minutely divided brown powder, which shows metallic lustre when pressed with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended appears of a blackish-blue color by transmitted light.

9. If to a solution of gold, potassa or soda be added in excess, it remains clear; on addition of *tannic acid* to the alkaline liquid a deep black precipitate of protoxide of gold (Au O) is formed, which separates perfectly after a little time.

§ 130.

b. Binoxide of Platinum (PtO_2).

1. Metallic platinum has a light steel-gray color; it is very lustrous, moderately hard, very malleable and ductile, difficultly fusible; it does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids. It dissolves in nitrohydrochloric acid, especially upon heating. The solution contains bichloride of platinum.

2. Binoxide of platinum is a blackish-brown, its hydrate a reddish-brown powder. Both are reduced by heat; they are both readily soluble in hydrochloric acid, and difficultly soluble in oxygen acids. Hydrated protoxide of platinum is black, and when heated, yields metallic platinum.

3. The salts of binoxide of platinum are decomposed at a red heat. They are yellow; bichloride of platinum is reddish-brown, its solution reddish-yellow, which tint it retains up to a high degree of dilution. The solution reddens litmus-paper. Exposure to a very low red heat converts bichloride of platinum to protochloride; application of a stronger red heat reduces it to the metallic state. Solution of bichloride of platinum, containing protochloride, has a dark-brown color.

4. *Hydrosulphuric acid* throws down from acid and neutral solutions—(but not from alkaline solutions, or, at all events, not completely)—after the lapse of some time a blackish-brown precipitate of bisulphide of platinum (PtS_2). If the solution is heated after the addition of the hydrosulphuric acid the precipitate forms *immediately*. It dissolves in a great excess of alkaline sulphides, more particularly of the higher degrees of sulphuration. Bisulphide of platinum is insoluble in hydrochloric acid and in nitric acid; but it dissolves in nitrohydrochloric acid.

5. *Sulphide of ammonium* produces the same precipitate; this redissolves slowly and with difficulty, but at last completely in a large excess of the precipitant, if the latter contains an excess of sulphur. Acids reprecipitate the bisulphide of platinum unaltered from the red-brown solution.

6. *Chloride of potassium* and *chloride of ammonium* (and also potassa and ammonia in presence of hydrochloric acid), produce in not too highly dilute solutions of salts of platinum, yellow crystalline precipitates of platinchlorides of potassium and ammonium. From dilute solutions these precipitates are obtained by evaporating with chloride of potassium or chloride of ammonium on the water-bath to dryness, and treating the residue with dilute spirit of wine until the alkaline chlorides are dissolved. The precipitates are no more soluble in acids than in water, they dissolve, however, by heating with soda or potassa-lye. Upon ignition platinchloride

of ammonium leaves spongy platinum behind. Platinchloride of potassium leaves platinum and chloride of potassium, but its decomposition is only complete when it is gently heated in a stream of hydrogen gas, or ignited with oxalic acid.

7. *Protochloride of tin* imparts to solutions of salts of binoxide of platinum which contain much free hydrochloric acid an INTENSELY DARK BROWNISH-RED COLOR, owing to a reduction of the binoxide or bichloride of platinum to protoxide or simple chloride. But the reagent produces no precipitate in such solutions.

8. *Sulphate of protoxide of iron* does not precipitate solution of bichloride of platinum, unless the two are boiled together for a long time, when metallic platinum separates.

§ 131.

Recapitulation and remarks.—The reactions of gold and platinum enable us, at least partially, to detect these two metals in the presence of many other oxides, and also when platinum and gold are present in the same solution. In the latter case the solution is evaporated to dryness with chloride of ammonium, and the residue treated with spirit of wine, in order to obtain the gold in solution, and the platinum in the residue. The latter yields metallic platinum on ignition, while gold may be thrown down from the solution after evaporating off the alcohol, by means of protosulphate of iron.

SECOND DIVISION OF THE SIXTH GROUP.

Special Reactions.

§ 132.

a. PROTOXIDE OF TIN (Sn O).

1. TIN has a light gray-white color and a high metallic lustre; it is soft and malleable; when bent, it produces a crackling sound. When heated in the air, it absorbs oxygen, and is converted into grayish-white binoxide; heated on charcoal before the blowpipe, it forms a white coating on the support. Concentrated hydrochloric acid dissolves tin to protochloride, with evolution of hydrogen gas; nitrohydrochloric acid dissolves it, according to circumstances, to bichloride or to a mixture of proto- and bichloride. Tin dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into sulphate of binoxide; moderately concentrated nitric acid oxidizes it readily, particularly with the aid of heat; the white binoxide (hydrated metastannic acid $Sn O_2$, 2 H O) formed, does not redissolve in an excess of the acid.

2. PROTOXIDE OF TIN is a black or grayish-black powder; its hydrate is white. Protoxide of tin is reduced by fusion with

cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into hydrated metastannic acid, which is insoluble in an excess of the acid.

3. The SALTS OF PROTOXIDE OF TIN are colorless, and are decomposed by heat. The soluble salts, in the neutral state, redden litmus-paper. The salts of protoxide of tin rapidly absorb oxygen from the air, and are partially or entirely converted into salts of binoxide; hence a solution of protochloride of tin becomes speedily turbid (from ensuing separation of oxychloride of tin), if the glass is often opened and there is only little free acid present; hence it is only quite recently prepared protochloride of tin which will completely dissolve in water free from air, and the crystallized protochloride of tin dissolves to a clear liquid only in water acidified with hydrochloric acid.

4. *Hydrosulphuric acid* throws down from neutral and acid solutions of salts of protoxide of tin a dark brown precipitate of hydrated PROTOSULPHIDE OF TIN (Sn S), which is insoluble, or nearly so, in protosulphide of ammonium, but dissolves readily in the higher yellow sulphide. Acids precipitate from this solution yellow bisulphide of tin, mixed with sulphur. Protosulphide of tin dissolves also in solution of soda or potassa. Acids precipitate from these solutions brown protosulphide. Boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid gas; boiling nitric acid converts it into insoluble hydrated metastannic acid. Alkaline solutions of protosalts of tin are not, or at least only imperfectly, precipitated by hydrosulphuric acid.

5. *Sulphide of ammonium* produces the same precipitate of hydrated PROTOSULPHIDE OF TIN.

6. *Soda*, *potassa*, *ammonia*, *carbonate of potassa*, and *carbonate of ammonia* produce in solutions of salts of protoxide of tin a white, bulky precipitate of HYDRATE OF PROTOXIDE OF TIN (Sn O, H O), which redissolves readily in an excess of soda or potassa, but is insoluble in an excess of the other precipitants. If the solution of hydrate of protoxide of tin in potassa is briskly evaporated, a compound of binoxide of tin and potassa is formed, which remains in solution, whilst metallic tin precipitates; but upon evaporating slowly, crystalline anhydrous protoxide of tin separates.

7. *Terchloride of gold* produces in solutions of protochloride or protoxide of tin, upon addition of some nitric acid (without application of heat), a precipitate or coloration of PURPLE OF CASSIUS. (Compare § 129. 7.)

8. Solution of *chloride of mercury*, added in excess, produces in solutions of protochloride of tin or of protoxide of tin in hydrochloric acid, a white precipitate of SUBCHLORIDE OF MERCURY, owing to the protosalt of tin withdrawing from the chloride of mercury half of its chlorine.

9. If a fluid containing protoxide or protochloride of tin and hydrochloric acid is added to a mixture of *ferricyanide of potassium* and *sesquichloride of iron*, a precipitate of *Prussian blue* (ferrocyanide of iron, $Fe_4\ Cfy_3$) separates immediately, owing to the reduction of the ferricyanide ($Fe_4\ Cfy_4$*$+ 2\ H\ Cl + 2\ Sn\ Cl = Fe_4\ Cfy_3 + H_2\ Cfy + 2\ Sn\ Cl_2$). This reaction is extremely delicate, but it can be held to be decisive only in cases where no other reducing agent is present.

10. If compounds of protoxide of tin, mixed with *carbonate of soda* and some *borax*, or, better still, with a mixture of equal parts of *carbonate of soda* and *cyanide of potassium*, are exposed on a charcoal support to the *inner blowpipe flame*, malleable grains of METALLIC TIN are obtained. The best way of making quite sure of the real nature of these grains, is to triturate them and the surrounding parts of charcoal with water forcibly in a small mortar; then to wash the charcoal off from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support, the latter becomes covered with a coating of white binoxide.

§ 133.

b. BINOXIDE OF TIN ($Sn\ O_2$).

1. BINOXIDE OF TIN is a powder varying in color from white to straw-yellow, and which upon heating transiently assumes a brown tint. It forms two different series of compounds with acids, bases, and water. The hydrate precipitated by alkalies from solution of bichloride of tin dissolves readily in hydrochloric acid; whilst that formed by the action of nitric acid upon tin—hydrate of metastannic acid—remains undissolved. If the hydrated metastannic acid be boiled a short time with hydrochloric acid, it unites with the latter; on pouring off the excess of hydrochloric acid and adding water the compound dissolves. The aqueous solution of the common bichloride of tin is not altered by addition of strong hydrochloric acid, while this reagent throws down from the aqueous solutions of metabichloride of tin, the latter salt as a white precipitate. The color of solution of common bichloride of tin is not altered by protochloride of tin; solution of metabichloride of tin becomes yellow by addition of the latter. From the dilute solutions of both the bichlorides of tin, the corresponding hydrates of the binoxide are thrown down on boiling.

2. The SALTS OF BINOXIDE OF TIN are colorless; they are decomposed at a red heat. The soluble salts of binoxide of tin, in the neutral state, redden litmus paper. Anhydrous bichloride of tin is a volatile liquid, strongly fuming in the air.

3. *Hydrosulphuric acid* throws down from all acid and neutral

* $(2\ Fe_2\ Cfdy) = Fe_4\ Cfy_4$, because $Cfdy = C_{12}\ N_6\ Fe_2 = 2\ Cfy$.

solutions of salts of binoxide of tin, particularly upon heating, a *white* flocculent precipitate, if the solution of the binoxide is in excess; a *dull-yellow* precipitate, if the hydrosulphuric acid is in excess. The former (the white precipitate) may be assumed, in the case of a solution of bichloride of tin, to consist of chloro-bisulphide of tin (however, it has not as yet been analysed); the latter (the yellow precipitate) consists of hydrated BISULPHIDE OF TIN ($Sn S_2$). Alkaline solutions are not precipitated by hydrosulphuric acid. The precipitation is prevented by a very large excess of hydrochloric acid. The bisulphide of tin dissolves readily in potassa, alkaline sulphides, concentrated boiling hydrochloric acid and aqua regia. It dissolves with some difficulty in pure ammonia, and is nearly insoluble in carbonate of ammonia. Nitric acid converts it into insoluble binoxide of tin. It is insoluble in solution of acid sulphite of potassa. Upon deflagrating bisulphide of tin with nitrate and carbonate of soda, sulphate of soda and binoxide of tin are obtained. If a solution of bisulphide of tin in potassa is boiled with teroxide of bismuth, tersulphide of bismuth and binoxide of tin are formed, which latter substance remains dissolved in the potassa solution.

4. *Sulphide of ammonium* produces the same precipitate of hydrated BISULPHIDE OF TIN; the precipitate redissolves readily in an excess of the precipitant. From this solution acids reprecipitate the bisulphide of tin unaltered.

5. *Soda*, *potassa* and *ammonia*, *carbonate of soda* and *carbonate of ammonia*, produce in solutions of salts of binoxide of tin white precipitates which, according to the nature of the solutions, consist of hydrate of binoxide of tin, or of hydrate of metastannic acid. Both dissolve readily in an excess of potassa.

6. *Sulphate of soda*, *nitrate of ammonia* (in fact, most neutral salts), when added in excess, throw down from solutions of both modifications of binoxide of tin, provided they are not too acid, the whole of the tin as HYDRATED BINOXIDE OR HYDRATE OF METASTANNIC ACID. Heating promotes the precipitation: $Sn Cl_2 + 4 Na O, S O_3 + 4 H O = Sn O_2 2 H O + Na Cl + 2 (Na O, H O, 2 S O)$.

7. *Metallic zinc* precipitates from solutions of bichloride of tin, in the absence of free acid, in the first place, some metallic tin, then white oxychloride; but in presence of a sufficient quantity of free hydrochloric acid, METALLIC TIN, in the shape of small gray scales, or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference between tin and antimony).

8. The compounds of the binoxide of tin manifest the same deportment before the blowpipe as those of the protoxide. Binoxide of tin is also readily reduced when fused with cyanide of potassium in a glass tube.

§ 134.

c. Teroxide of Antimony (Sb_2O_3).

1. Metallic antimony has a bluish tin-white color and is very lustrous; it is hard, brittle, readily fusible. When heated on charcoal before the blowpipe, it emits thick white fumes of teroxide of antimony, which form a coating on the coal; this combustion continues for some time, even after the removal of the metal from the flame; it is the most distinctly visible if a current of air is directed with the blowpipe directly upon the sample on the charcoal. But if the sample on the support is kept steady, that the fumes may ascend straight, the metallic grain becomes surrounded with a net of brilliant crystals of teroxide of antimony. Nitric acid oxidizes antimony readily; the dilute acid converting it almost entirely into teroxide, the more concentrated acid into antimonic acid; both are nearly insoluble in nitric acid; still in the acid fluid filtered from the precipitate there are always found traces of antimony. Hydrochloric acid, even boiling, does not attack antimony. In nitrohydrochloric acid the metal dissolves readily. The solution contains terchloride of antimony ($Sb Cl_3$), or pentachloride of antimony ($Sb Cl_5$), according to the degree of concentration of the acid and the duration of the action.

2. According to the different modes of its preparation, Teroxide of Antimony occurs either in the form of white, brilliant crystalline needles, or as a grayish-white powder. It fuses at a moderate red heat; when exposed to a higher temperature, it volatilizes without decomposition. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. Boiled with hydrochloric acid (free from chlorine) and with iodide of potassium (free from iodic acid) iodine is not liberated (*Bunsen*). Teroxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

3. Antimonic acid (Sb_2O_5) is pale yellow; its hydrates are white. Both the acid and its hydrates redden litmus-paper; they are slightly soluble in water, and almost insoluble in nitric acid, but dissolve pretty readily in hot concentrated hydrochloric acid: the solution contains pentachloride of antimony ($Sb Cl_5$), and turns turbid upon addition of water. Antimonic acid when boiled with hydrochloric acid and iodide of potassium liberates iodine which dissolves in the hydriodic acid present, giving a brown color to the liquid. Upon ignition, antimonic acid loses oxygen, and is converted into antimonate of teroxide of antimony (Sb_2O_3, Sb_2O_5). Of the antimonates the potassa and ammonia salts alone are soluble in water: acids precipitate hydrate of antimonic acid from the solutions, chloride of sodium throws down from them antimonate of soda (§ 93.2.)

4. Most of the SALTS OF TEROXIDE OF ANTIMONY are decomposed upon ignition; the haloid salts volatilize readily and unaltered. The soluble neutral salts of antimony redden litmus-paper. When treated with a large amount of water, they are decomposed into insoluble basic salts and acid solutions containing teroxide of antimony. Thus, for instance, water throws down from solutions of terchloride of antimony in hydrochloric acid, a white bulky precipitate of OXYTERCHLORIDE OF ANTIMONY (powder of Algaroth) $Sb Cl_3$ 5 $Sb O_3$, which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and therefore prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the oxyterchloride of antimony is distinguished from the basic salts of bismuth formed under similar circumstances.

5. *Hydrosulphuric acid* precipitates from acid solutions of teroxide of antimony the whole of the metal unless a very large excess of free (mineral) acid be present as orange-red TERSULPHIDE OF ANTIMONY ($Sb S_3$). In alkaline solutions this reagent fails to produce a precipitate or, at least, it precipitates them only imperfectly; neutral solutions also are only imperfectly thrown down by it. The tersulphide of antimony produced is readily dissolved by potassa and by alkaline sulphides, especially if the latter contain an excess of sulphur; it is but sparingly soluble in ammonia, and—if it contains no free sulphur nor pentasulphide of antimony—almost insoluble in bicarbonate of ammonia. It is insoluble in dilute acids. Concentrated boiling hydrochloric acid dissolves it, with evolution of hydrosulphuric acid gas. It is not dissolved by an aqueous solution of acid sulphite of potassa.

When heated in the air, the precipitate is converted into a mixture of antimonate of teroxide of antimony with tersulphide of antimony. When deflagrated with nitrate of soda, it gives sulphate and antimonate of soda. If a potassa solution of tersulphide of antimony is boiled with teroxide of bismuth, tersulphide of bismuth precipitates, and teroxide of antimony dissolved in potassa remains in the solution. On fusing tersulphide of antimony with cyanide of potassium, metallic antimony and sulphocyanide of potassium are produced. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbonic acid gas (see § 135, 12), no sublimate of antimony is produced. But if a mixture of tersulphide of antimony with carbonate of soda or with cyanide of potassium and carbonate of soda, is heated in a glass tube in a stream of hydrogen gas (compare § 135, 4), a mirror of antimony is deposited on the inner surface of the tube, immediately behind the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid, sulphuretted hydrogen throws down pentasulphide of antimony (Sb

S_3), which dissolves readily when heated with solution of soda or ammonia, and equally so in concentrated boiling hydrochloric acid with evolution of hydrosulphuric acid gas and separation of sulphur. It is very slightly soluble in cold solution of bicarbonate of ammonia.

6. *Sulphide of ammonium* produces in solutions of teroxide of antimony an orange-red precipitate of TERSULPHIDE OF ANTIMONY, which readily dissolves in an excess of the precipitant if the latter contains an excess of sulphur. Acids throw down from this solution pentasulphide of antimony ($Sb S_5$). However, the orange color appears in that case usually of a lighter tint, owing to an admixture of free sulphur.

7. *Soda, potassa, ammonia, carbonate of soda*, and *carbonate of ammonia* throw down from solutions of terchloride of antimony, and also of simple salts of teroxide of antimony—but far less completely and usually after the lapse of some time, from solutions of tartar emetic or analogous compounds—a white; bulky precipitate of TEROXIDE OF ANTIMONY, which redissolves pretty readily in an excess of soda or potassa, but requires the application of heat for its re-solution in carbonate of soda, and is altogether insoluble in ammonia.

8. *Metallic Zinc* precipitates from all solutions of teroxide of antimony, if they contain no free nitric acid, METALLIC ANTIMONY as a black powder. If a few drops of a solution of antimony, containing some free hydrochloric acid, are poured into a platinum dish (the inside of a platinum crucible cover), and a small piece of zinc introduced, hydrogen is evolved and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions; these new reactions I can therefore recommend as being delicate and characteristic. Cold hydrochloric acid fails to remove the stain, which, however, may be immediately removed by warm nitric acid.

9. If a solution of teroxide of antimony in solution of potassa or soda is mixed with solution of *nitrate of silver*, a deep black precipitate of SUBOXIDE OF SILVER forms with the grayish-brown precipitate of oxide of silver. Upon now adding ammonia in excess, the oxide is redissolved, whilst the suboxide is left undissolved (*H. Rose*). The following equation will explain the formation of the suboxide of silver in this process: $K O, Sb O_3 + 4 Ag O = K O, Sb O_5 + 2 Ag_2 O$. This exceedingly delicate reaction affords us an excellent means of detecting teroxide of antimony in presence of antimonic acid.

10. If a solution of teroxide of antimony is introduced into a flask in which hydrogen gas is being evolved from pure *zinc* and dilute *sulphuric acid*, the zinc oxidizes not only at the expense of the oxygen of the water, but also at the expense of that of the ter-

oxide of antimony, and the antimony separates accordingly in the metallic state; but a portion of the metal combines in the moment of its separation with the liberated hydrogen of the water, forming ANTIMONETTED HYDROGEN GAS ($Sb H_3$). If this operation is conducted in a gas-evolution flask, connected by means of a perforated cork with the limb of a bent tube of which the other limb ends in a fine orifice,* and the hydrogen passing through the fine aperture of the tube is ignited after the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating in a state of intense ignition upon the combustion of the antimonetted hydrogen; white fumes of teroxide of antimony rise from the flame, which condense readily upon cold substances, forming spots on them which are not dissolved by water. But if a cold body, a porcelain dish, for instance, is now depressed into the flame, METALLIC ANTIMONY is deposited upon the surface of the plate, in a state of the most minute division, forming a deep black and almost lustreless spot. If the middle part of the tube through which the gas is passing is heated to redness, the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part.

As the acids of arsenic give under the same circumstances similar spots of metallic arsenic, it is always necessary to examine the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With spots deposited in a porcelain dish the object in view is most readily attained by treating them with a solution of chloride of soda (a compound of hypochlorite of soda with chloride of sodium, prepared by mixing a solution of chloride of lime with carbonate of soda in excess, and filtering); which will immediately dissolve arsenical spots, leaving the spots proceeding from antimony untouched, or, at least, removing them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it whilst the current of hydrogen gas still continues to pass through the tube: if the mirror volatilizes only at a higher temperature, and the hydrogen gas then issuing from the tube does not smell of garlic; if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing fuses to small lustrous globules distinctly discernible through a magnifying glass,—the presence of antimony may be considered certain. Or, better still, the metals may be identified by conducting through the tube a *very slow* stream of dry hydrosulphuric acid gas, and heating the mirror, by means of a spirit-lamp, proceeding from the outer to the inner border, and accordingly in an opposite direction

* In accurate experiments it is advisable to use *Marsh's* apparatus. (§ 135, 10).

to that of the gaseous current. The antimonial mirror is by this means converted into tersulphide of antimony, which appears of a more or less reddish-yellow color, and almost black when in thick layers. If a feeble stream of dry hydrochloric acid gas is now transmitted through the glass tube, the tersulphide of antimony, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker, it takes a short time to dissipate it. The reason for this is, that the tersulphide of antimony decomposes readily with hydrochloric acid, and the terchloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water, the presence of antimony in the latter fluid may readily be proved by means of hydrosulphuric acid. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

The deportment of antimonetted hydrogen towards a solution of nitrate of silver is noticed in § 137, 6.

11. If a mixture of a compound of antimony with *carbonate of soda and cyanide of potassium* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognised by the peculiar appearances attendant upon their oxidation (compare § 134, 1).

§ 135.

d. ARSENIOUS ACID ($As O_3$).

1. METALLIC ARSENIC has a blackish-gray color and high metallic lustre, which it retains in dry air, but loses in moist air, becoming covered with suboxide; the metallic arsenic of commerce looks therefore rather dull, the planes of crystallization appearing bronze-colored and feebly shining. Arsenic is not very hard, but brittle: at a dull red heat it volatilizes without fusion. The fumes have a most characteristic odor of garlic, which proceeds from the suboxide of arsenic formed. Heated with free access of air, arsenic burns—at an intense heat with a bluish flame—emitting white fumes of arsenious acid, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized, and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror); a very thin coating of the sublimate appears of a brownish-black color. In contact with air and water arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat, into arsenious acid, which dissolves only sparingly in an excess of the acid; strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid; concentrated boiling

sulphuric acid oxidizes it to arsenious acid, with evolution of sulphurous acid.

2. ARSENIOUS ACID generally presents the appearance either of a transparent vitreous or of a white porcelain-like mass. Triturated, it gives a heavy, white, gritty powder. When heated, it volatilizes in white inodorous fumes. If the operation is conducted in a glass tube, a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious acid is only difficu[illegible]pistened by water; it comports itself in this respect like a [illegible]stance. It is difficultly soluble in cold, but more readily i[illegible]. It is copiously dissolved by hydrochloric acid, as we[illegible]tion of soda and potassa. Upon boiling with nitroh[illegible] acid it dissolves to arsenic acid. It is highly poisonou[illegible]

3. The ARSENITES are mostly decomposed [illegible]tion either into arsenates and metallic arsenic, which vo[illegible]or into arsenious acid and the base with which it wa[illegible]ned. Of the arsenites those only with alkaline bases are s[illegible]in water. The insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Terchloride of arsenic is a colorless, volatile liquid, fuming in the air, which allows the addition of a little water, but is decomposed by a larger amount into arsenious acid, which partly separates, and hydrochloric acid, which retains the rest of the arsenious acid in solution. On heating and concentrating a solution of arsenious acid in hydrochloric acid, pentachloride of arsenic esapes with the vapors.

4. *Hydrosulphuric acid* colors yellow the aqueous solutions of arsenious acid without causing a precipitate. It also does not precipitate the neutral arsenites, but on adding one of the stronger acids, there separates at once bright yellow TERSULPHIDE OF ARSENIC (sulpharsenious acid). It is also produced in the hydrochloric solution of arsenites that are insoluble in water. The formation of this precipitate is not prevented, even by a great excess of hydrochloric acid. Alkaline solutions are not precipitated. The tersulphide of arsenic is easily and completely soluble in hydrates, carbonates, bicarbonates, and sulphides of the alkalies. Hydrochloric acid, even when concentrated and hot, scarcely attacks it. It is easily decomposed and dissolved by boiling nitric acid.

If recently precipitated tersulphide of arsenic is digested with sulphurous acid and acid sulphite of potassa, the precipitate is dissolved; upon heating the solution to boiling, the fluid turns turbid, owing to the separation of sulphur, which upon continued boiling is for the greater part redissolved. The fluid contains, after expulsion of the sulphurous acid, arsenite and hyposulphite of potassa: $2\,As\,S_3 + 8\,(KO, 2\,SO_2) = 2\,(KO, As\,O) + 6\,(KO, S\,O_2) + 3\,S + 7\,SO_2$. Tersulphide of antimony and bisulphide of tin do not show this reaction, as already stated (§ 133, 3 and 134, 5).—*Bunsen.*

The deflagration of tersulphide of arsenic with carbonate of soda and nitrate of soda gives rise to the formation of arsenate and sulphate of soda. If a solution of tersulphide of arsenic in potassa is boiled with hydrated carbonate or basic nitrate of teroxide of bismuth, tersulphide of bismuth and arsenite of potassa are produced. If a mixture of tersulphide of arsenic with from 3 to 4 parts of carbonate of soda is made into a paste with some water, and this spread over small glass splinters, and after being well dried, rapidly heated to redness in a glass tube through which dry hydrogen gas is transmitted, a large portion of the arsenic present is reduced to the metallic state and expelled, if the temperature applied is sufficiently high. Part of the reduced arsenic forms a metallic mirror on the inner surface of the tube, the remainder is carried away suspended in the hydrogen gas; the minute particles of arsenic impart a bluish tint to the flame when the gas is kindled, and form stains of arsenic upon the surface of a porcelain dish depressed upon the flame. The fusion of the mixture of tersulphide of arsenic with carbonate of soda first gives rise to the formation of a double tersulphide of arsenic and sulphide of sodium (sulpharsenite of sulphide of sodium), and of arsenite of soda: $2\ As\ S_3 + 4\ (Na\ O, CO_2) = 3\ (Na\ S, As\ S_3) + Na\ O, As\ O_3 + 4\ C\ O_2$. Upon heating these products the arsenite of soda is resolved into arsenic and arsenate of soda ($5\ As\ O_3 = 2\ As + 3\ As\ O_5$), and the tersulphide of arsenic and sulphide of sodium into arsenic and pentasulphide of arsenic and sulphide of sodium ($5\ As\ S_3 = 2\ As + 3\ As\ S_5$); and by the action of the hydrogen the arsenate of soda is also converted into hydrate of soda, arsenic, and water. With the exception, therefore, of that portion of the arsenic which constitutes a component part of the double pentasulphide of arsenic and sulphide of sodium formed in the process, a sulphur salt which is not decomposed by hydrogen, all the arsenic is expelled.—(*H. Rose.*)

This method of reduction gives indeed very accurate results, but it does not enable us to distinguish arsenic from antimony with a sufficient degree of certainty, nor to detect the one in presence of the other. (Compare § 134, 5.)

The operation is conducted in the apparatus illustrated by Fig. 26. *a* is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the mixture of tersulphide of arsenic and carbonate of soda is placed; this tube is made of difficultly fusible glass free from lead. When the apparatus is completely filled with pure hydrogen gas, *d* is exposed to a gentle heat at first, in order to expel all the moisture which may still be present, and then suddenly to a very intense heat,* to

* The flame of the blowpipe or of the Bunsen lamp with chimney, answers the purpose best.

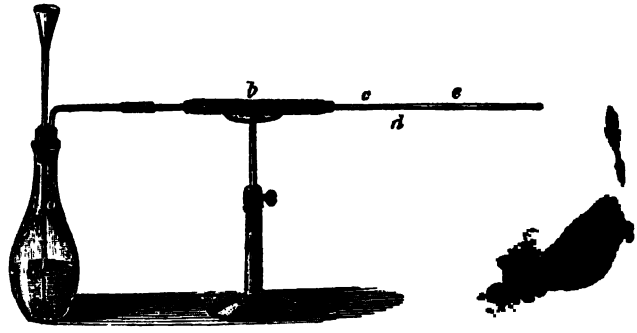

Fig. 26.

prevent the sublimation of undecomposed tersulphide of arsenic. The metallic mirror is deposited near the point *e*. Another method of effecting the reduction of tersulphide of arsenic to the metallic state, and which combines with the very highest degree of delicacy the advantage of precluding the possibility of confounding arsenic with antimony, will be found described in number 12.

5. *Sulphide of ammonium* also causes the formation of TERSULPHIDE OF ARSENIC. In neutral and alkaline solutions, however, the tersulphide formed does not precipitate, but remains dissolved as a double sulphide of arsenic and ammonium (sulpharsenite of sulphide of ammonium). From this solution it precipitates immediately upon the addition of a free acid.

6. *Nitrate of silver* leaves aqueous solutions of arsenious acid clear, or at most produces only a trifling yellowish-white turbidity in them; but if a little ammonia is added, a yellow precipitate of ARSENITE OF SILVER ($3\ Ag\ O, As\ O_3$) separates. The same precipitate forms, of course, immediately upon the addition of nitrate of silver to the solution of a neutral arsenite. The precipitate dissolves readily in nitric acid as well as in ammonia, and is not insoluble in nitrate of ammonia; if therefore a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the nitrate of ammonia formed.

7. *Sulphate of copper* produces under the same circumstances as the nitrate of silver a yellowish-green precipitate of ARSENITE OF COPPER.

8. If to a solution of arsenious acid in an excess of concentrated solution of soda or potassa, or to the solution of an alkaline arsenite mixed with *caustic potassa* or *soda* a few drops of a dilute solution of sulphate of copper are added, a clear, blue fluid is obtained, which upon boiling deposits a red precipitate of SUBOXIDE OF COPPER, leaving arsenate of potassa in solution. This reaction is

exceedingly delicate, provided not too much of the solution of sulphate of copper be used. Even should the red precipitate of suboxide of copper be so exceedingly minute as to escape detection by transmitted light, yet it will always be discernible with great distinctness upon looking in at the top of the test tube. Of course this reaction, although really of great importance in certain instances, as a confirmatory proof of the presence of arsenious acid, and more particularly also as a means of distinguishing that acid from arsenic acid, is yet entirely inapplicable for the *direct detection* of arsenic, since grape sugar and other organic substances also produce suboxide of copper from salts of oxide of copper in the same manner.

9. If a solution of arsenious acid mixed with hydrochloric acid is heated with a clean slip of *copper*, an IRON-GRAY film is deposited on the copper, even in *highly dilute* solutions; when this film increases in thickness, it peels off in black scales. If the coated copper slip is heated with solution of ammonia, the film peels off from the copper, and separates in form of minute spangles (*Reinsch*). It is to be observed that this coating is not pure arsenic, but an arsenide of copper (Cu_5As). On heating the dried compound, a relatively small part of the arsenic volatilizes (in the open tube arsenious acid is formed), and an alloy rich in copper remains behind. (*Fresenius, Lippert.*) Reinsch's test is only conclusive when the coating of the copper slip is demonstrated to contain arsenic, since antimony and other metals are precipitated on copper under similar circumstances, with much the same appearance.

10. If an acid or neutral solution of arsenious acid or any of its compounds is mixed with *zinc*, *water*, and *diluted sulphuric acid*, ARSENETTED HYDROGEN (AsH_3) is formed, in the same manner as compounds of antimony give under analogous circumstances antimonetted hydrogen. (Compare § 134, 10.) This reaction affords us a means for the detection of even the most minute quantities of arsenic.

The operation is conducted in the apparatus illustrated by Fig. 27, or in one of similar construction.* *a* is the evolution flask; *b* a bulb intended to receive the water mechanically carried along with the gaseous current; *c* a tube filled with cotton and small lumps of chloride of calcium to remove the last traces of water. This tube is connected with *b* and *d* by vulcanized india-rubber which must be freed from adhering sulphur by warming for some time in solution of soda; *d* should have an inner diameter of about one-fourth of an inch (see Fig. 28), and must be made of difficultly fusible

* I willingly adopt the very convenient form of *Marsh's* apparatus recommended by *Otto* in his excellent *Manual of Chemistry*.

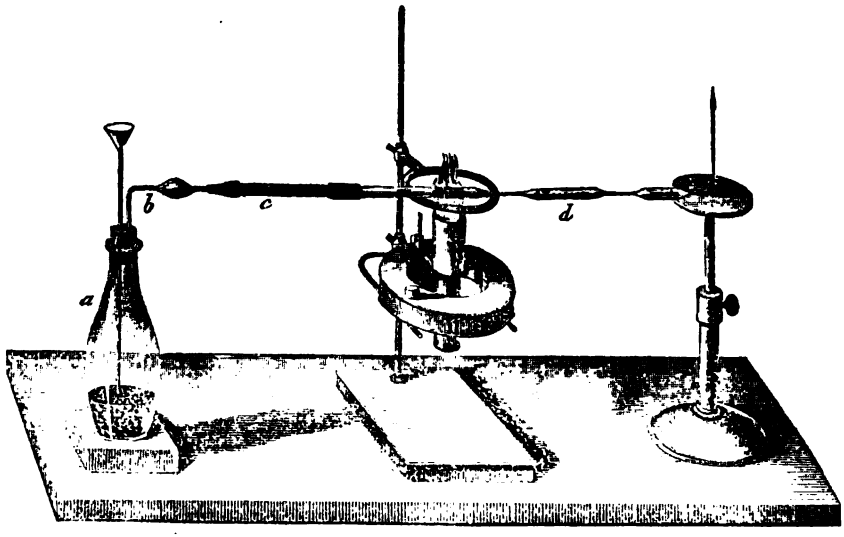

Fig. 27

glass free from lead. In experiments requiring great accuracy the tube should be drawn out as shown in Fig. 27. The operation is now commenced by evolving in *a* a somewhat rapid current of hydrogen gas, from pure granulated zinc and a *previously cooled* mixture of 1 part of concentrated sulphuric acid with 3 parts of water, to which a few drops of bichloride of platinum are advantageously added. When the evolution of hydrogen has proceeded for some time, so that it may safely be concluded the air has been completely expelled from the apparatus, the gas is kindled at the open end of the tube *d*. It is advisable to wrap a piece of cloth round the flask before kindling the gas, to guard against accidents in case of an explosion. It is now absolutely necessary first to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is done by depressing a porcelain dish horizontally into the flame to half the depth of the latter: if the hydrogen contains arsenetted hydrogen, brownish or brownish-black stains of arsenic will appear on the porcelain; the non-appearance of such stains may be considered as a proof of the freedom of the zinc and sulphuric acid from arsenic. In very accurate experiments, however, additional evidence is required to ensure the positive certainty of the purity of the reagents employed; for this purpose the part of the tube *d*, shown in Fig. 27, is heated to redness with a *Berzelius* or gas-lamp, and kept some time in a state of ignition: if no arsenical coating makes its appearance in the narrowed part of the tube, the reagents employed may be pro-

Fig. 28.

nounced free from arsenic,* and the operation proceeded with, by pouring the fluid to be tested for arsenic through the funnel tube into the flask, and afterwards some water to rinse the tube. Only a very little of the fluid ought to be poured in at first, as in cases where the quantity of arsenic present is considerable, and a somewhat large supply of the fluid is poured into the flask, the evolution of gas often proceeds with such violence as to stop the further progress of the experiment.

Now if the fluid contains arsenic, there is immediately evolved, with the hydrogen, arsenetted hydrogen, which at once imparts a bluish tint to the flame of the kindled gas, owing to the combustion of the particles of arsenic separating from the arsenetted hydrogen in passing through the flame. At the same time white fumes of arsenious acid arise, which condense upon cold objects. If a porcelain capsule is now depressed into the flame, the separated and not yet reoxidized arsenic condenses upon the plate in black stains, the same way as antimony. (See § 134, 10.) The stains formed by arsenic incline, however, more to a blackish-brown tint, and show a bright metallic lustre; whilst the antimonial stains are of a deep black color and but feebly lustrous. The arsenical stains may be distinguished moreover from the antimonial stains by solution of chloride of soda (compare § 134, 10), which will at once dissolve arsenical spots, leaving antimonial spots unaffected, or removing them only after a considerable time.

If the heat of a *Berzelius*, or gas-lamp, is now applied to the part of the tube *d*, shown in Fig. 27, a brilliant arsenical mirror makes its appearance in the narrowed portion of the tube behind the heated part; this mirror is of a darker and less silvery white hue than that produced by antimony under similar circumstances; from which it is, moreover, distinguished by the facility with which it may be dissipated in a current of hydrogen gas without previous fusion, and by the characteristic odor of garlic emitted by the escaping (unkindled) gas. If the gas is kindled whilst the mirror in the tube is being heated, the flame will, even with a very weak current of gas, deposit arsenical stains on a porcelain plate.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic with positive certainty in presence of antimony. Now, in cases of this kind, the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic:—

Heat the long tube through which the arsenetted hydrogen

* [If no mirror is obtained in 10 to 15 minutes the materials are pure enough for toxical examinations. It is scarcely possible, however, to obtain reagents so free from arsenic as not to give a faint arsenical mirror in an hour or two.]

passes to redness in several parts, to produce distinct metallic mirrors; then transmit through the tube a very weak stream of dry hydrosulphuric acid gas, and heat the metallic mirrors with a common spirit-lamp, proceeding from the outer towards the inner border. If arsenic alone is present, yellow tersulphide of arsenic is formed inside the tube; if antimony alone is present, an orange-red or black tersulphide of antimony is produced; and if the mirror consisted of both metals, the two sulphides appear side by side, the sulphide of arsenic as the more volatile lying invariably beyond the sulphide of antimony. If you now transmit through the tube containing the sulphide of arsenic, sulphide of antimony, or both sulphides together, dry hydrochloric acid gas, without applying heat, no alteration will take place if sulphide of arsenic alone is present, even though the gas be transmitted through the tube for a considerable time. If sulphide of antimony alone is present, this will entirely disappear, as already stated, and if both sulphides are present, the sulphide of antimony will immediately volatilize, whilst the yellow sulphide of arsenic will remain. If a small quantity of ammonia is now drawn into the tube, the sulphide of arsenic is dissolved, and may thus be readily distinguished from sulphur which perhaps may have separated. My personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic.

The deportment of arsenetted hydrogen towards solution of nitrate of silver is described § 137, 6.

Marsh was the first who suggested the method of detecting arsenic by the production of arsenetted hydrogen.

11. If a small lump of arsenious acid (*a*) be introduced into the pointed end of a drawn-out glass tube (Fig. 29) and a fragment of very recently burnt charcoal (*b*) pushed down the tube to within a short distance of the arsenious acid, and the flame of a spirit-lamp applied, first to the piece of charcoal, then to the arsenious acid, a MIRROR OF METALLIC ARSENIC will form at *c*, owing to the reduction of the arsenious acid vapor by the red-hot charcoal. If the tube be now cut between *b* and *c*, and then heated in an inclined position, with the cut end *c* turned upwards, the metallic mirror will volatilize, emitting the characteristic odor of garlic. This is both the simplest and safest way of recognizing pure arsenious acid.

12. If arsenites, or arsenious acid, or tersulphide of arsenic are fused together with a mixture of equal parts of dry *carbonate of soda* and *cyanide of potassium*, the whole of the arsenic is reduced to the metallic state, and so is the base also, if easily reducible; the eliminated oxygen converts part of the cyanide of potassium into cyanate of potassa. In the reduction of tersulphide of arsenic, sulphocyanide of potassium is formed. The operation is conducted as follows:—introduce the perfectly dry arsenical compound into

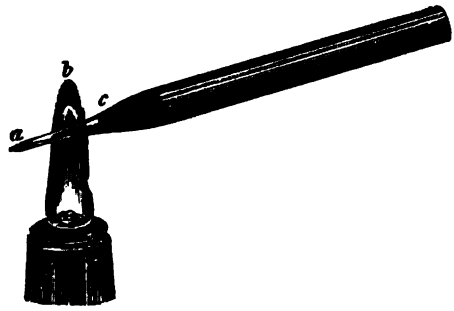

Fig. 29.

the bulb of a small bulb-tube (Fig. 30), and cover it with six times the quantity of a perfectly dry mixture of equal parts of carbonate of soda and cyanide of potassium. The whole quantity must not much more than half fill the bulb, otherwise the fusing cyanide of potassium is likely to ascend into the tube. Heat the bulb now gently with a gas or spirit-lamp; should some water still escape upon gently heating the mixture, wipe the inside of the tube *perfectly dry* with a twisted slip of paper. It is of the highest importance for the success of the experiment to bestow great care upon the expulsion of the water, drying the mixture, and wiping the tube clean and dry. Apply now a strong heat to the bulb, to effect the reduction of the arsenical compound, and continue this for awhile, as the arsenic often requires some time for its complete

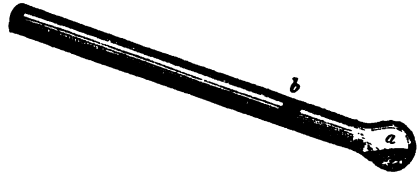

Fig. 30.

sublimation. The mirror, which is deposited at *b*, is of exceeding purity. It is obtained from all arsenites whose bases remain either altogether untouched, or are reduced to such metallic arsenides as lose their arsenic partly or totally upon the simple application of heat. This method deserves to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by it, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for the direct production of arsenic from tersulphide of arsenic, and is in this respect superior in simplicity and accuracy to all other methods hitherto suggested. The delicacy of the reaction

may be very much heightened by heating the mixture in a stream of dry carbonic acid gas. A series of experiments made by *Dr. V. Babo* and myself has shown that the most accurate and satisfactory results are obtained in the following manner:—

Figs. 31 and 32 show the apparatus in which the process is conducted.

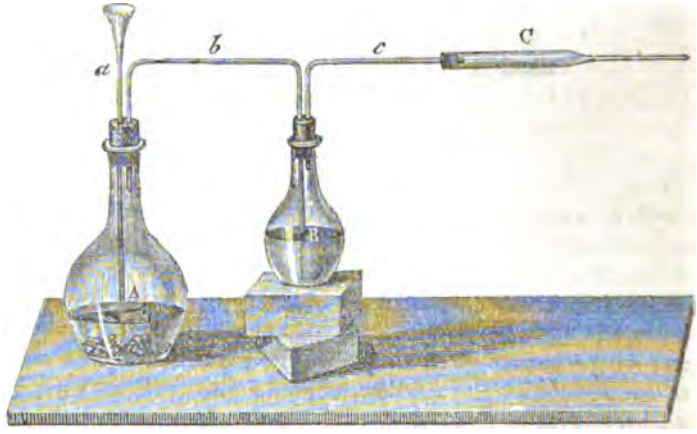

Fig. 31.

A is a capacious flask intended for the evolution of carbonic acid; it is half-filled with water and lumps of solid limestone or marble (not chalk, as this would not give a constant stream of gas). *B* is a smaller flask containing concentrated sulphuric acid. The flask *A* is closed with a doubly-perforated cork, into the one aperture of which is inserted a funnel-tube (*a*), which reaches nearly to the bottom of the flask; into the other perforation is fitted a tube (*b*), which serves to conduct the evolved gas into the sulphuric acid in *B*, where it is thoroughly freed from moisture. The tube *c* conducts the dried gas into the reduction-tube *C*, of which Fig. 32 give a representation on the scale of one-third of the actual length. The tube may have an inner diameter of about three-eighths of an inch.

Fig. 32.

When the apparatus is fully prepared for use, triturate the perfectly dry sulphide of arsenic, or arsenite, in a slightly heated mortar with about twelve parts of a well-dried mixture consisting of three parts of carbonate of soda and one part of cyanide of potassium. Put the powder upon a narrow slip of paper bent into the shape of a gutter, and push this into the reduction-tube down

to *e*; turn the tube now half-way round its axis, which will cause the mixture to drop into the tube between *e* and *d*, every other part remaining perfectly clean. Connect the tube now with the gas-evolution apparatus, and evolve a moderate stream of carbonic acid, by pouring some hydrochloric acid into the flask *A*. Heat the tube *C* in its whole length very gently with a spirit-lamp, until the mixture in it is quite dry; when every trace of water is expelled, and the gas-stream has become so slow that the single bubbles pass through the sulphuric acid in *B* at intervals of one second, heat the reduction-tube to redness at *c*, by means of a spirit or gas-lamp; when *c* is red-hot, apply the flame of a second gas or larger spirit-lamp to the mixture, proceeding from *d* to *e*, until the whole of the arsenic is expelled. The far greater portion of the volatilized arsenic recondenses at *h*, whilst a small portion only escapes through *i*, imparting to the surrounding air the peculiar odor of garlic. Advance the flame of the second lamp slowly and gradually up to *c*, by which means the whole of the arsenic which may have condensed in the wide part of the tube is driven to *h*. When you have effected this, close the tube at the point *i* by fusion, and apply heat, proceeding from *i* towards *h*, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner perfectly distinct mirrors of arsenic are produced from as little as the $\frac{1}{350}$th part of a grain of tersulphide of arsenic. No mirrors are obtained by this process from tersulphide of antimony, nor from any other compound of antimony.

13. If arsenious acid or one of its compounds is exposed on a charcoal support to the *reducing flame of the blowpipe*, a highly characteristic garlic odor is emitted, more especially if some carbonate of soda is added to the examined sample. This odor has its origin in the reduction and re-oxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the mere indications of the sense of smell, *cannot be implicitly relied on.*

§ 136.

e. Arsenic Acid ($As O_5$)

1. Arsenic acid is a transparent or white mass, which gradually deliquesces in the air, and dissolves slowly but in large quantity in water. It fuses at a gentle red heat without suffering decomposition; but at a higher temperature it is resolved into oxygen and arsenious acid, which volatilizes. It is highly poisonous.

2. Most of the arsenates are insoluble in water. Of the so-called neutral arsenates those with alkaline bases alone are soluble in water. Most of the neutral and basic arsenates can bear a

strong red heat without suffering decomposition. The acid arsenates lose their excess of acid upon ignition, the free acid being resolved into arsenious acid and oxygen.

3. *Hydrosulphuric acid* fails to precipitate alkaline and neutral solutions of arsenates; but in acidified solutions it causes at first, a reduction of arsenic to arsenious acid, with simultaneous separation of sulphur, and then throws down tersulphide of arsenic. This process goes on, until finally, all the arsenic is precipitated as As_2S_3 mixed with 2 S.—(*Wackenroder*, *Ludwig*, *H. Rose.*)

The precipitate never forms instantaneously, and in dilute solutions frequently only after the lapse of a considerable time (twenty-four hours, for instance). Heating (to about 160° Fah.) promotes its separation. If a solution of arsenic acid, or of an arsenate, is mixed with sulphurous acid, or with sulphite of soda and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; application of heat promotes the change. If hydrosulphuric acid is now added, the whole of the arsenic is thrown down at once as tersulphide.

4. *Sulphide of ammonium* converts the arsenic acid in neutral and alkaline solutions of arsenates into PENTASULPHIDE OF ARSENIC (As_2S_5), which remains in solution as ammonio-pentasulphide of arsenic (sulpharsenate of sulphide of ammonium). Upon the addition of an acid to the solution, this double sulphide is decomposed, and pentasulphide of arsenic precipitates. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arsenates are precipitated with hydrosulphuric acid. It is promoted by heat. This precipitate is really As_2S_5 and not a mixture of As_2S_3 with 2 S.

5. *Nitrate of silver* produces under the circumstances stated § 135, 6, a highly characteristic reddish-brown precipitate of ARSENATE OF SILVER ($3\,AgO, AsO_5$), which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in nitrate of ammonia. Accordingly, if a part of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to reproduce the precipitate.

6. *Sulphate of copper* produces under the circumstances stated § 135, 7, a greenish-blue precipitate of ARSENATE OF COPPER ($2\,CuO, HO, AsO_5$).

7. When a dilute solution of arsenic acid to which a little hydrochloric acid has been added, is heated with metallic *copper*, the latter remains perfectly unaltered. If, however, the liquid is mixed with twice its volume of concentrated hydrochloric acid, the copper acquires a gray coating as described under arsenious acid. The reaction under the circumstances above described is as sensitive as in the presence of arsenious acid (*Reinsch*).

8. With *zinc* in presence of sulphuric acid, with *cyanide of*

potassium, and before the *blowpipe*, the compounds of arsenic acid comport themselves in the same way as those of arsenious acid. If the reduction of arsenic acid by zinc is effected in a platinum dish, the platinum does not turn black, as is the case in the reduction of antimony by zinc (§ 134, 8).

9. If a solution of arsenic acid, or of an arsenate soluble in water, is added to a clear mixture of *sulphate of magnesia*, *chloride of ammonium** and a sufficient quantity of *ammonia*, a crystalline precipitate of ARSENATE OF AMMONIA AND MAGNESIA (2 Mg O, N H_4 O, As O_5 + 12 aq.) separates; from concentrated solutions immediately, from dilute solutions after some time.

If a portion of the precipitate be dissolved in a few drops of nitric acid, a drop of nitrate of silver added, and into the mixture be placed a glass rod previously dipped in ammonia, brown-red arsenate of silver is formed (distinction of arsenate from phosphate of ammonia-magnesia).

§ 137.

Recapitulation and remarks.—I will here describe first the different ways best adapted to effect the detection or separation of tin, antimony, and arsenic, when present together in the same compound or mixture, and afterwards the most trustworthy means of distinguishing between the several oxides of each of the three metals.

1. If you have a mixture of sulphide of tin, sulphide of antimony, and sulphide of arsenic, triturate 1 part of it, together with 1 part of dry carbonate of soda, and 1 part of nitrate of soda, and transfer the mixed powder gradually to a small porcelain crucible containing 2 parts of nitrate of soda kept in a state of fusion at a not overstrong heat; oxidation of the sulphides ensues, attended with slight deflagration. The fused mass contains binoxide of tin, arsenate and antimonate of soda, with sulphate, carbonate, nitrate, and nitrite of soda. You must take care not to raise the heat to such a degree, nor continue the fusion so long, as to lead to a reduction of the nitrite of soda to the caustic state so that soluble stannate of soda be not formed. Treat the fused mass, poured out upon a piece of porcelain and pulverized, with *a little cold* water until it is completely softened; then filter the fluid off from the undi-

[* The operator will save time and avoid mistakes by keeping among his reagents the mixture here alluded to, which is often needed in testing for arsenic and phosphoric acids. It is properly prepared by dissolving in water 24.6 grammes of crystallized sulphate of magnesia and 33 grammes of chloride of ammonium (the commercial salts will answer), adding some ammonia and diluting to the volume of a *litre*. From the mixture thus made no hydrate of magnesia separates by addition of more ammonia. If a precipitate (sesquioxide of iron, &c.) should form, filter off and use the clear solution.]

solved residue, which contains the binoxide of tin and antimonate of soda. Mix the filtrate, which contains the arsenate of soda and the other salts, with nitric acid to distinctly acid reaction, and heat to expel carbonic and nitrous acids, then with a sufficient proportion of solution of nitrate of silver; a precipitate of chloride of silver forms (if the reagents employed or the precipitated sulphides contained a chlorine compound). Filter, and carefully add to the filtrate dilute solution of ammonia, whereupon the presence of *arsenic* is manifested by the characteristic reddish-brown precipitate of arsenate of oxide of silver which makes its appearance, first in the uppermost stratum of the fluid where the solution of ammonia comes first into contact with it, but subsequently, upon complete neutralization of the free acid, in every part of the fluid. Arsenic may also be tested by a mixture of sulphate of magnesia, chloride of ammonium and ammonia, see § 136, 9.

Wash now the filter containing the residuary binoxide of tin and antimonate of soda once with water, then three times with a mixture of equal parts of water and spirit of wine. Transfer the residue into a small platinum capsule (or a porcelain capsule into which a piece of platinum foil is placed), and heat gently with some hydrochloric acid. The mass either dissolves entirely, or in case much tin is present, a white precipitate remains. Add now a fragment of zinc. Both tin and antimony are reduced, and the presence of *antimony* is at once made evident by the black stain which appears upon the platinum. When the evolution of hydrogen has nearly ceased, what remains of the zinc is removed, and the contents of the capsule are heated with a little hydrochloric acid, antimony remains undissolved in black flocks, while *tin* goes into solution as protochloride. In the filtered solution, the tin may now be detected by chloride of mercury or a mixture of sesquichloride of iron and ferricyanide of potassium; while the antimony, after washing with water, may be dissolved in a little nitrohydrochloric acid and further tested by hydrosulphuric acid. This method of separation is further detailed in § 192.

2. If the mixed sulphides, after removing the greater share of the water that adheres to them by placing the filter on blotting-paper, are treated with warm fuming hydrochloric acid, the sulphide of antimony and sulphide of tin dissolve, whilst the sulphide of arsenic is left nearly altogether undissolved. If the residuary sulphide of arsenic is treated with ammonia, and the solution obtained evaporated, after adding to it a very little carbonate of soda, an arsenical mirror may readily be produced from the residue with cyanide of potassium and carbonate of soda in a stream of carbonic acid gas. The solution, which contains the tin and antimony, may be treated as directed in 1.

Or, if there is a considerable excess of antimony, the solution

may be mixed with sesquicarbonate of ammonia in excess, and boiled. A considerable proportion of the antimony present dissolves in this process, whilst binoxide of tin mixed with a small quantity of teroxide of antimony remains undissolved. The presence of the tin may now be the more readily proved by the method given in 1 (*Bloxam*).

3. On digesting the mixed sulphides with some solid sesquicarbonate of ammonia and water at a gentle heat, sulphide of arsenic dissolves, while the sulphides of antimony and tin remain behind. This separation is not, however, complete, a trace of sulphide of antimony easily passes into solution, and some sulphide of arsenic remains in the residue. It is, therefore, necessary to examine the precipitate which is thrown down by acidifying the alkaline solution with hydrochloric acid, especially when it is in small quantity, by dissolving it, after washing, in ammonia, evaporating with a little carbonate of soda and igniting the residue with a mixture of cyanide of potassium and carbonate of soda in a stream of carbonic acid. A metallic mirror thus obtained is decisive proof of the presence of arsenic. The residue insoluble in carbonate of ammonia is to be examined according to 2.

4. If sulphide of antimony, sulphide of tin, and sulphide of arsenic are dissolved in sulphide of potassium, a *large* excess of a concentrated solution of sulphurous acid added, the mixture digested for some time in the water-bath, then boiled until all sulphurous acid is expelled, and filtered, the filtrate contains all the arsenic as arsenious acid (which may be precipitated from it by hydrosulphuric acid), whilst tersulphide of antimony and bisulphide of tin are left behind undissolved (*Bunsen*). After dissolving the residue in hydrochloric acid, the antimony and tin may be detected as directed in 2.

5. In the analysis of alloys, binoxide of tin and teroxide of antimony are often obtained together as a residue insoluble in nitric acid. This is best treated by fusing the dried mass with hydrate of soda in a silver crucible, softening the contents of the crucible with water and adding to the solution one-third its volume of alcohol. The whole is now brought upon a filter, antimonate of soda remains upon the latter and is to be washed with weak alcohol to which a few drops of solution of carbonate of soda have been added.—The filtrate is acidified with hydrochloric acid, and tin and arsenic are thrown down by hydrosulphuric acid with the aid of heat. The sulphides thus obtained are heated in a current of hydrosulphuric acid gas, when all the tin remains behind as bisulphide, while all sulphide of arsenic volatilizes and may be collected in ammonia (*H. Rose*).

6. For the most accurate way of separating antimony and arsenic, and distinguishing between the two metals, viz., by treating

in close vessels volatilizes only at a bright red heat; in the air it sublimes at low redness and condenses in the form of transparent needles and plates. The unignited substance dissolves in ordinary acids, yielding colorless solutions, which in contact with *zinc* or *tin*, become first blue, then green, and finally black under separation of protoxide. By digesting with *copper* the solution in sulphuric acid acquires a blue, that in hydrochloric acid acquires a brown color. The reaction is often not perceptible until after the lapse of some time. *Ferrocyanide of potassium* produces a reddish-brown precipitate, *infusion of galls* a green precipitate. *Hydrosulphuric acid*, when added in small proportion, imparts a blue tint to solutions of molybdic acid; when added in larger proportion, it produces a brownish-black precipitate; the fluid over the latter at first appears green, but after standing some time, and upon application of heat with renewed transmission of hydrosulphuric acid gas through the liquid, all the molybdenum may be finally thrown down as brownish-black tersulphide of molybdenum ($Mo S_3$). The precipitated tersulphide of molybdenum dissolves in sulphides of the alkali metals; acids reprecipitate from the sulphur salts the sulphur acid ($Mo S_3$). Warming facilitates the separation. When roasted at a red-heat in the air or heated with nitric acid, sulphide of molybdenum is converted into molybdic acid.

Molybdic acid dissolves readily in solutions of pure *alkalies* and *carbonates of the alkalies*; from rather concentrated solutions, *nitric*, and *hydrochloric* acids throw down molybdic acid, which redissolves upon further addition of the precipitant. The solutions of molybdates of the alkalies are colored yellow by *hydrosulphuric acid*, and give afterwards, upon addition of acids, a brownish-black precipitate. For the deportment of molybdic acid with phosphoric acid and ammonia, see § 145, 10.

[By putting a fragment of zinc into a hydrochloric solution of molybdic acid or of a molybdate, adding a few drops of strong solution of *sulphocyanide of potassium* and finally a few drops of sulphuric or hydrochloric acid, so that a gentle evolution of hydrogen is excited, the liquid shortly acquires a carmine color. The reaction is very delicate.—(*Braun.*) To recognize molybdenum in presence of sesquioxide of iron and peroxide of nitrogen, which likewise give a red color with sulphocyanide of potassium, the solution is treated with sulphurous acid or an alkaline sulphite and hydrochloric acid, until no coloration is produced in it by sulphocyanide of potassium alone. Sesquioxide of iron is thus reduced to protoxide, and peroxide of nitrogen to a lower oxide. On now adding solution of sulphocyanide of potassium and a fragment of zinc, the reaction at once becomes manifest.—(*Editor.*)]

[Solutions of molybdic acid acidified with dilute hydrochloric acid impart a brown tint to turmeric paper.—(*A. Müller.*) (Compare zirconia and boracic acid).]

When molybdic acid is heated on charcoal in the oxidizing flame it volatilizes: at the same time the support acquires a yellow, often crystalline coating, which becomes white on cooling. In the reducing flame metallic molybdenum is formed, which may be obtained as a gray powder on washing the pulverized charcoal. Sulphide of molybdenum when heated in the oxidizing flame yields sulphurous acid gas and a sublimate of molybdic acid.

c. OXIDES OF TUNGSTEN.—Tungsten is of rare occurrence, the commonest minerals containing it are Scheelite (tungstate of lime) and Wolfram (tungstate of protoxides of iron and manganese). Tungsten as obtained by the reduction of tungstic acid in a stream of hydrogen gas at a strong red heat, is a very difficultly fusible, iron-gray powder. Ignited in the air pulverulent tungsten is converted into tungstic acid ($W O_3$), heated to redness in chlorine gas it yields a sublimate of red chloride ($W Cl_2$): the latter decomposes with water into hydrochloric acid and oxide of tungsten ($W O_2$), which on exposure to air absorbs oxygen and is converted into the blue tungstate of tungsten ($W O_2$, $W O_3$). Tungsten is not dissolved by acids, not even by aqua regia. It is also insoluble in solution of potassa, but dissolves in a mixture of potassa with hypochlorite of an alkali. Oxide of tungsten is black, when strongly

ignited in the air it is converted into tungstic acid. Tungstic acid is a lemon-yellow, non-volatile powder, insoluble in water and acids. By fusing it with bisulphate of potassa and treating the fused mass with water, there is at first obtained an acid solution free from tungstic acid. After its removal, the residual tungstate of potassa dissolves. Tungstates of the alkalies are obtained with difficulty by boiling tungstic acid with solutions of alkaline carbonates: by fusing the acid with the carbonates, the tungstates of potassa and soda are easily prepared. They are soluble in water. *Hydrochloric, nitric,* and *sulphuric acids* throw down from solutions of tungstates white precipitates which are insoluble in excess of acid (distinction from molybdic acid); but soluble in ammonia. By evaporating tungstates to dryness with excess of hydrochloric acid and treating the residue with water, tungstic acid remains undissolved. *Chlorides of barium* and *calcium*, and *nitrates of silver* and *protoxide of mercury* throw down white precipitates. *Ferrocyanide of potassium* on addition of some acid gives with solutions of tungstates a brown-red coloration, and after some time, a brown-red precipitate. *Tincture of galls*, by addition of an acid, throws down a brown precipitate. *Hydrosulphuric acid* scarcely affects acid solutions; *sulphide of ammonium* does not precipitate alkaline solutions; but by acidifying the latter light-brown sulphide of tungsten (WS_3) separates, which is somewhat soluble in pure water, but is insoluble in saline solutions. *Protochloride of tin* gives a yellow precipitate; if the mixture be acidified with hydrochloric acid and heated, it acquires a fine blue color (characteristic and sensitive reaction). By supersaturating the solution of an alkaline tungstate with hydrochloric, or, better, with phosphoric acid and adding *zinc*, a fine blue color is obtained. *Microcosmic salt* dissolves tungstic acid: in the oxidizing flame the bead is clear, colorless or yellowish: in the reducing flame it becomes blue and by addition of protosulphate of iron, blood-red. Heated with a very little soda in the reducing flame on charcoal, tungsten is obtained as a powder which may be separated by washing the pulverized charcoal. The tungstates which are insoluble in water are mostly decomposed by acids. Wolfram, which is difficultly decomposed by acids, may be fused with carbonate of soda. Water extracts tungstate of soda from the fused mass.

d. OXIDES OF TELLURIUM.—Tellurium is found native, alloyed with other elements, and in the form of tellurous acid. It is extremely rare. It is a white, brittle, easily fusible metal; may be sublimed in a glass tube; heated in the air it burns with a greenish-blue flame with production of dense white vapors of tellurous acid. Tellurium is insoluble in hydrochloric acid; but in nitric acid readily dissolves to tellurous acid (TeO_2). Tellurium in the state of powder, dissolves in strong sulphuric acid with purple color: on addition of water it is thrown down from this solution. Tellurous acid is white, fuses at a moderate heat to a yellow liquid, is volatile in the air at a strong red heat, does not yield a crystalline sublimate. The anhydrous acid easily dissolves in hydrochloric acid, to a slight extent in nitric acid, largely in caustic potassa, slowly in ammonia, and is nearly insoluble in water. Hydrated tellurous acid is white, perceptibly soluble in cold water, soluble in hydrochloric and nitric acids. Water throws down from the solutions the white hydrate: from the solution in nitric acid crystallized anhydrous tellurous acid separates after some time. *Alkalies and alkaline carbonates* precipitate from the hydrochloric solution, white hydrate which is soluble in excess of the precipitant. *Hydrosulphuric acid* throws down from acid solutions, brown sulphide of tellurium (TeS_2) which is readily soluble in sulphide of ammonium. *Sulphite of soda, protochloride of tin* and *zinc* precipitate metallic tellurium as a black powder. Telluric acid (TeO_3) is obtained by fusing tellurium or tellurites with nitrate and carbonate of soda. The fused mass is insoluble in water; it remains clear in the cold after acidifying with hydrochloric acid; but on boiling evolves chlorine with formation of tellurous acid; the liquid therefore now gives a precipitate with water if the excess of acid be not too great.

When tellurium, its sulphides or oxides are fused with *cyanide of potassium* in a stream of hydrogen, tellurocyanide of potassium is formed. The fused mass is soluble in water, a stream of air precipitates from it all the tellurium (distinction and separation from selenium). Tellurous or telluric acid fused with *carbonate of potassa* and *charcoal*, yields telluride of potassium from which acids evolve telluretted hydrogen as a fetid gas. Compounds of tellurium, when mixed with carbonate of soda and subjected to the inner blowpipe flame, suffer reduction and volatilize. The vapors of tellurium oxidize again in the outer flame and coat the charcoal support with a white incrustation of tellurous acid.

e. SELENIUM exists sparingly in nature in combination with various metals. It is sometimes found in the flue-dust of roasting furnaces, and in Nordhausen oil-of-vitriol. It is on the one hand, related to tellurium; on the other, to sulphur; and thus stands on the boundary between the metals and non-metallic elements. In the fused state it has a gray-black color, it volatilizes and sublimes at high temperatures, and when heated in the air burns with a characteristic odor of decaying horse-radish, to selenious acid ($Se O_2$). It dissolves, without oxidizing, in strong sulphuric acid and is precipitated by dilution, in red flocks. It is dissolved and oxidized by nitric and nitrohydrochloric acids to selenious acid. Selenious acid, when produced by sublimation, forms white four-sided needles; its hydrate gives crystals resembling those of nitrate of potassa. Both dissolve readily in water, producing a strongly acid liquid; of the neutral selenites only those with alkaline base are soluble in water; their solutions react alkaline; selenites of lead and silver dissolve with difficulty—all other selenites dissolve with ease, in nitric acid. *Hydrosulphuric acid* in presence of hydrochloric acid, produces in solutions of selenious acid or of selenites a precipitate (sulphide of selenium), which is yellow in cold and reddish-yellow in hot solutions, and is soluble in sulphide of ammonium. In neutral solutions of selenites *chloride of barium* yields a white precipitate of selenite of baryta which is soluble in hydrochloric or nitric acid. *Protochloride of tin* or *sulphurous acid* on addition of hydrochloric acid, produce a red, or in hot liquids, a gray precipitate of selenium. Selenic acid is formed by heating selenium or its compounds with nitrate and carbonate of soda. The fused mass is soluble in water; treated with hydrochloric acid it remains clear, on boiling, it evolves chlorine while selenic acid is reduced to selenious acid.—Selenium and its compounds when fused with *cyanide of potassium* in a current of hydrogen gas, yield selenocyanide of potassium from which selenium does not separate by the action of air (distinction from tellurium); by continued boiling with hydrochloric acid selenium is, however, precipitated. On charcoal in the reducing flame, selenium compounds emit the highly characteristic odor of decaying horse-radish above mentioned, which serves for their ready detection.

B.—DEPORTMENT OF THE ACIDS AND THEIR RADICALS WITH REAGENTS.

§ 139.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the bases, into GENERAL REAGENTS, *i. e.*, such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, *i.e.*, such as serve to effect the detection and identification of the INDIVIDUAL ACIDS. The groups into which we classify the various acids can scarcely be defined and limited with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those

of INORGANIC and ORGANIC ACIDS. We base this division upon those characteristics by which, irrespectively of theoretical considerations, the ends of analysis are most easily attained. We select therefore here, as the characteristic mark to guide us in the classification into organic and inorganic acids, the deportment which the various acids manifest at a high temperature, and call *organic* those acids of which the salts—(particularly those which have an alkali or an alkaline earth for base)—are decomposed upon ignition, the decomposition being attended with separation of carbon.

By selecting this deportment at a high temperature as the distinctive characteristic of organic acids, we are enabled to determine at once by a most simple preliminary experiment the class to which an acid belongs. The salts of organic acids with alkalies or alkaline earths are converted into carbonates when heated to redness.

Before proceeding to the special study of the several acids considered in this work, I give here, the same as I have done with the bases, a general view of the whole of them classified in groups.

CLASSIFICATION OF ACIDS IN GROUPS.

I. INORGANIC ACIDS.

FIRST GROUP:

Division *a*. *Chromic acid* (sulphurous and hyposulphurous acids, iodic acid).

Division *b*. *Sulphuric acid* (hydrofluosilicic acid).

Division *c*. *Phosphoric acid, boracic acid, oxalic acid, hydrofluoric acid* (phosphorous acid).

Division *d*. *Carbonic acid, silicic acid.*

SECOND GROUP:

Chlorine and *hydrochloric acid, bromine* and *hydrobromic acid, iodine* and *hydriodic acid, cyanogen* and *hydrocyanic acid* together with *hydroferro-* and *hydroferricyanic acids, sulphur* and *hydrosulphuric acid* (nitrous, hypochlorous, chlorous and hypophosphorous acids).

THIRD GROUP:

Nitric acid, chloric acid (perchloric acid).

II. ORGANIC ACIDS.

FIRST GROUP:

Oxalic acid, tartaric acid, citric acid, malic acid (racemic acid).

SECOND GROUP:

Succinic acid, benzoic acid.

THIRD GROUP:

Acetic acid, formic acid (propionic acid, butyric acid, lactic acid).

The acids which are printed in italics are the most important from their frequent occurrence in the various natural or industrial subjects of chemical investigation: the others are comparatively rare.

I. Inorganic Acids.

§ 140.

First Group.

Acids which are precipitated from Neutral Solutions by Chloride of Barium.

This group is again subdivided into four divisions, viz.:

1. Acids which are decomposed in acid solution by hydrosulphuric acid, and to which attention has therefore been directed already in the testing for bases, viz., CHROMIC ACID, *sulphurous acid*, and *hyposulphurous acid*, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts; and also *iodic acid*.*

2. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta compounds of which are insoluble in hydrochloric acid, SULPHURIC ACID (*hydrofluosilicic acid*).

3. Acids which are not decomposed in an acid solution by hydrosulphuric acid, and the baryta compounds of which dissolve in hydrochloric acid, apparently WITHOUT DECOMPOSITION, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation; PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, and HYDROFLUORIC ACID (*phosphorous acid*). (*Oxalic acid* belongs more properly to the organic group. We consider it, however, here with the acids of the inorganic class, as the property of its salts to be decomposed upon ignition without actual carbonization may lead to its being overlooked as an organic acid.)

4. Acids which are not decomposed in acid solution by hydrosulphuric acid, and the baryta salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION (separation of the acid); CARBONIC ACID, SILICIC ACID.

First Division of the First Group of the Inorganic Acids.

§ 141.

Chromic Acid ($Cr O_3$).

1. CHROMIC ACID presents the appearance of a scarlet-red crystalline mass, or of distinct acicular crystals. Upon ignition it is

* All the oxides of the sixth group of metals which possess decided acid characters, viz., *arsenic*, *antimonic*, *selenious* and *selenic acids*, properly belong to the first division of the first group of acids. On account, however, of their deportment towards hydrosulphuric acid they are most conveniently considered in connection with the bases.

resolved into sesquioxide of chromium and oxygen. It deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-brown tint, which remains still visible in very dilute solutions.

2. The CHROMATES are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition; those with alkaline bases are fixed, and soluble in water; the solutions of the neutral alkaline chromates are yellow, those of the alkaline bichromates are red. These tints are still visible in highly dilute solutions. The yellow color of the solution of a neutral salt changes to red on the addition of a mineral acid, owing to the formation of an acid chromate.

3. *Hydrosulphuric acid* acts upon acidified solutions of chromates producing at first a brown and finally a green coloration of the liquid whereby a salt of sesquioxide of chromium is formed with simultaneous separation of sulphur, which gives to the solution a milky appearance ($KO, 2\ Cr\ O_3 + 4\ SO_3 + 3\ HS = KO, SO_3 + Cr_2\ O_3, 3\ SO_3 + 3\ HO + 3\ S$). The reaction is facilitated by warming, when a portion of the sulphur is oxidized to sulphuric acid.

4. Chromic acid may also be reduced to sesquioxide of chromium by means of many other substances, and more particularly by *sulphurous acid*, or by heating with *hydrochloric acid*, especially upon the addition of alcohol (in which case chloride of ethyle and aldehyde are evolved); also by *metallic zinc*, or by heating with *tartaric acid*, *oxalic acid*, &c. All these reactions are clearly characterized by the change of the red or yellow color of the solution to the green tint of the salt of sesquioxide of chromium.

5. *Chloride of barium* produces in aqueous solutions of chromates a yellowish-white precipitate of CHROMATE OF BARYTA (Ba O, Cr O_3), which is soluble in dilute hydrochloric acid and nitric acid.

6. *Nitrate of silver* produces in aqueous solutions of chromates a dark purple-red precipitate of CHROMATE OF SILVER (Ag O, Cr O_3), which is soluble in nitric acid and in ammonia; in feebly acid solutions it produces a precipitate of BICHROMATE OF SILVER (Ag O, 2 Cr O_3).

7. *Acetate of lead* throws down from aqueous or acetic solutions of a chromate a yellow precipitate of CHROMATE OF LEAD (Pb O, Cr O_3), which is soluble in potassa, but only difficultly soluble in dilute nitric acid, and is insoluble in acetic acid. Upon heating with alkalies, the yellow neutral salt is converted into basic red chromate of lead (2 Pb O, Cr O_3).

8. On placing at the bottom of a tube 6 to 8 cubic centimetres of a dilute acid solution of *binoxide of hydrogen** pouring upon

* To be prepared by pulverizing a fragment of binoxide of barium of the size of a pea, with a little water, and gradually adding the same with stirring to a mixture

it a layer of ether ¼ of an inch in depth and adding finally a solution containing chromic acid, the binoxide of hydrogen immediately assumes a fine blue color. On closing the tube with the thumb and reversing its position several times without violent agitation the solution is decolorized, while the ether becomes blue.

The latter phenomenon is especially characteristic. One part of chromate of potash in 40000 parts of water gives a perceptible reaction (*Storer*); vanadic acid impairs its delicacy (*Werther*); compare § 116, 2. The blue coloration is doubtless due to a compound of chromic acid and binoxide of hydrogen, and not to the formation of a higher acid of chromium. After some time the ether becomes colorless, the chromic acid suffering reduction to sesquioxide of chromium.

9. If insoluble chromates are fused together with *carbonate of soda* and *nitrate of soda*, and the fused mass is treated with water, the fluid produced appears YELLOW from the alkaline chromate which it holds in solution; upon the addition of an acid the yellow color changes to red. The oxides remain behind either in the pure state or as carbonates, if they are not soluble in the caustic soda formed from the nitrate.

10. Chromates (not containing metallic oxides giving colored beads) give the same reactions with *borax* and *microcosmic salt* in the blowpipe flame as are exhibited by sesquioxide of chromium (§ 105).

Remarks.—When testing for bases, we always find the chromic acid as sesquioxide of chromium, since hydrosulphuric acid reduces it to that state. The characteristic color of the solution frequently renders the application of any further test unnecessary. The reactions with salts of silver and salts of lead afford positive and confirmatory proof of the presence of chromic acid in aqueous solutions. Acid solutions are tested with binoxide of hydrogen.

More rarely occurring Acids of the First Division.

§ 142.

a. Sulphurous acid (SO_2) is a colorless, uninflammable gas, which exhales the stifling odor of burning sulphur. It dissolves copiously in water. The solution has the odor of the gas, reddens litmus paper, and bleaches Brazil-wood paper. It absorbs oxygen from the air, and is thereby converted into sulphuric acid. The salts of sulphurous acid are colorless. Of the neutral sulphites those with alkaline base only are readily soluble in water; many of the sulphites insoluble or difficultly

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of about 30 c. c. of hydrochloric acid, and 120 c. c. of water. Instead of binoxide of barium the impure peroxide of sodium obtained by heating a piece of sodium in a porcelain capsule until it inflames, and then allowing it to burn completely, may be employed. The solution may be kept a long time without suffering decomposition.

soluble in water dissolve in an aqueous solution of sulphurous acid, but fall down again upon boiling. All the sulphites evolve sulphurous acid when treated with *sulphuric acid* or *hydrochloric acid*. *Chlorine water* dissolves most sulphites to sulphates. *Chloride of barium* precipitates neutral sulphites, but not free sulphurous acid. The precipitate dissolves in hydrochloric acid. *Hydrosulphuric acid* decomposes free sulphurous acid, water and pentathionic acid being formed and free sulphur eliminated, which latter separates from the fluid. If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from *zinc* and *hydrochloric acid*, hydrosulphuric acid is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of acetate of lead to which has been added a sufficient quantity of solution of soda to redissolve the precipitate which forms at first. Sulphurous acid is a powerful reducing agent; it reduces chromic acid, permanganic acid, chloride of mercury (to subchloride), decolorizes iodide of starch, produces a blue precipitate in a mixture of ferricyanide of potassium and sesquichloride of iron, &c. With a hydrochloric acid solution of *protochloride of tin*, a brown precipitate of PROTOSULPHIDE OF TIN is formed after some time.

When an aqueous solution of an alkaline sulphite is made just acid by acetic acid and poured into a relatively large amount of solution of *sulphate of zinc* mixed with a very little *nitroprusside of sodium* there is produced, when the quantity of sulphurous acid is not too small, a red color. If but a trace of sulphurous acid be present the color is developed by adding a little ferrocyanide of potassium. By addition of the latter substance a purple precipitate is thrown down if the sulphurous acid be not too small in amount (*Boedeker*). (Hyposulphites do not manifest this reaction.)

b. Hyposulphurous acid (S_2O_2). This acid does not exist in the free state. Its salts are generally soluble in water. The solutions of most hyposulphites may be boiled without suffering decomposition; hyposulphite of lime is resolved upon boiling into sulphite of lime and sulphur. If *Hydrochloric acid* or *sulphuric acid* is added to the solution of a hyposulphite, the fluid remains at first clear and inodorous, but after a short time—the shorter the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and exhales the odor of sulphurous acid. Application of heat promotes this decomposition. *Nitrate of silver* produces a white precipitate of HYPOSULPHITE OF SILVER, which is soluble in an excess of the hyposulphite; after a little while (upon heating almost immediately) the precipitate turns black, being decomposed into sulphide of silver and sulphuric acid. Hyposulphite of soda dissolves chloride of silver; upon the addition of an acid the solution remains clear at first, but shortly, and upon boiling immediately, sulphide of silver separates. *Chloride of barium* produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid.

When, as often happens, it is desired to test for sulphites and hyposulphites in presence of an alkaline sulphide, sulphate of zinc is added to the mixture until the alkaline sulphide is fully decomposed; the sulphide of zinc is filtered off, a portion of the filtrate is tested for hyposulphurous acid by addition of hydrochloric acid, another portion is treated with nitroprusside of sodium, &c., to detect sulphurous acid.

Iodic acid (IO_3). Iodic acid crystallizes in white, six-sided tables; at a moderate heat it is resolved into iodine vapor and oxygen; it is readily soluble in water. The salts are decomposed upon ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and metallic oxide; the iodates with an alkaline base alone dissolve readily in water. *Chloride of barium* throws down from solution of iodates of the alkalies a white precipitate of IODATE OF BARYTA, which is soluble in nitric acid; *nitrate of silver*, a white, granular-crystalline precipi-

tate of IODATE OF SILVER which dissolves readily in ammonia, but only sparingly in nitric acid. *Hydrosulphuric acid* throws down from solutions of iodic acid, with simultaneous separation of sulphur, IODINE, which then dissolves in hydriodic acid; if an excess of hydrosulphuric acid is added, the fluid loses its color, and sulphur separates, the iodine being converted into hydriodic acid. The iodates are likewise decomposed by hydrosulphuric acid. *Sulphurous acid* throws down IODINE, which upon addition of an excess of the acid is converted into hydriodic acid.

Second Division of the First Group of the Inorganic Acids.

§ 143.

SULPHURIC ACID (S O).

1. Anhydrous SULPHURIC ACID is a white, feathery-crystalline mass, which emits strong fumes upon exposure to the air; hydrated sulphuric acid forms an oily liquid, colorless and transparent like water. Both the anhydrous and hydrated acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydrous acid, with a hissing noise.

2. The neutral SULPHATES are easily soluble in water, with exception of the sulphates of baryta, strontia, lime and lead. The basic sulphates of many heavy metallic oxides are insoluble in water; but all dissolve in hydrochloric and nitric acids. The sulphates are mostly colorless or white. The sulphates of the alkalies are not decomposed by ignition. Of the other sulphates, some are decomposed easily, some with difficulty on ignition, and some altogether resist decomposition at high temperature.

3. *Chloride of barium* produces even in exceedingly dilute solutions of sulphuric acid and of the sulphates a finely-pulverulent, heavy, white precipitate of SULPHATE OF BARYTA (Ba O, S O_3), which is insoluble in dilute hydrochloric acid and in nitric acid. From very dilute solutions the precipitate separates only after standing some time. Concentrated acids and strong solutions of many salts, impair the delicacy of this reaction.

4. *Acetate of lead* produces a heavy, white precipitate of SULPHATE OF LEAD (Pb O, S O_3) which is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid.

5. The salts of sulphuric acid with the alkaline earths which are insoluble in water and acids are converted into CARBONATES, by fusion with *alkaline carbonates*. But the sulphate of lead is reduced to the state of PURE OXIDE when treated in this manner. Both the conversion of the former into carbonates, and the reduction of the latter to the state of oxide, are attended with the formation of an alkaline sulphate. The sulphates of the alkaline earths and

sulphate of lead, are also resolved into insoluble carbonates and soluble alkaline sulphate when boiled with concentrated solutions of carbonates of the alkalies (compare §§ 98, 99, 100).

6. Upon fusing sulphates with *carbonate of soda* on charcoal in the inner flame of the blowpipe, the sulphuric acid is reduced, and sulphide of sodium formed, which may be readily recognized by the odor of hydrosulphuric acid emitted upon moistening the sample and the part of the charcoal into which the fused mass has penetrated, and adding some acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water and some acid, a BLACK STAIN of sulphide of silver is immediately formed.

Remarks.—The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta, precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of baryta, since they redissolve immediately upon diluting the acid fluid with water.

In testing for sulphuric acid with chloride of barium, the operator should make the solution tolerably dilute; he should also add some hydrochloric acid, without which, certain salts, *e. g.* alkaline citrates, may entirely prevent the separation of sulphate of baryta. In case very dilute solutions are to be examined for sulphuric acid, they should be allowed to stand for several hours in a warm place, after addition of chloride of barium. To be certain that a precipitate is really sulphate of baryta it may be examined according to § 143,6.—To detect free sulphuric acid in presence of a sulphate, the fluid under examination is mixed with a very little cane-sugar, and the mixture evaporated to dryness in a porcelain dish at 212° Fah. If free sulphuric acid was present, a black residue remains, or, in the case of most minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way (*Runge*).

§ 144.

HYDROFLUOSILICIC ACID (H F, Si F_2).—Hydrofluosilicic acid is a very acid fluid; when evaporated on platinum, it volatilizes completely as fluoride of silicon and hydrofluoric acid. When evaporated on glass, it etches the latter. With bases it forms water and silico-fluorides of the metals, which are most of them soluble in water, redden litmus paper, and are resolved upon ignition into metallic fluorides and fluoride of silicon.

Chloride of barium forms a crystalline precipitate with hydrofluosilicic acid

(§ 98, 6). Chloride of strontium and acetate of lead form no precipitates with this acid; *salts of potassa* precipitate transparent GELATINOUS SILICO-FLUORIDE OF POTASSIUM; *ammonia* in excess precipitates HYDRATED SILICIC ACID, with formation of fluoride of ammonium. When metallic silico-fluorides are heated with concentrated *sulphuric acid*, a fuming mixture of hydrofluoric acid and fluoride of silicon escapes. If the experiment is conducted in a platinum vessel covered with glass, the glass is ETCHED (§ 149, 5). The bases remain as sulphates.

Third Division of the First Group of the Inorganic Acids.

§ 145.

a. PHOSPHORIC ACID ($P O_5$).

1. PHOSPHORUS is usually a colorless, transparent, solid body, of 2·089 specific gravity; it has a waxy appearance. Taken internally, it acts as a virulent poison. It fuses at 113°, and boils at 554° Fah. By the influence of light, phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air, at the common temperature, it exhales a characteristic, highly disagreeable odor, and gradually oxidizes into phosphorous and phosphoric acids. At the same time, heavy fumes are formed [which, according to *Meissner*, consist of antozone combined with water]. Exposed to the air in the dark, phosphorus appears luminous. Phosphorus very readily takes fire spontaneously, and burns with a luminous flame, being converted into phosphoric acid, which is dissipated for the most part in white fumes through the surrounding air. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily upon heating. The solutions contain at first, besides phosphoric acid, also phosphorous acid. Hydrochloric acid does not dissolve phosphorus; if phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphoretted hydrogen gas escapes.

When a substance containing unoxidized phosphorus, is placed at the bottom of a flask, in the body of which is hung, by means of a loosely fitting cork, a slip of filter-paper moistened with solution of nitrate of silver, and the whole is warmed to 85° to 100° Fah., the paper becomes black from the reducing action of even the minutest traces of phosphorus. If, when the reaction is complete, the blackened part of the paper is treated with boiling water, the liquid, after removal of silver by hydrochloric acid and filtration, gives on evaporation in the water-bath to a very small volume, a solution in which phosphoric acid may be detected by the tests below described (*J. Scherer*). It must not be forgotten that a blackening of paper saturated with silver solution, may also be produced by hydrosulphuric acid, formic acid, the volatile products

of putrefaction, &c. The detection of phosphoric acid in the slip of paper has no value as a test for phosphorus unless the paper be itself free from phosphates. The deportment of phosphorus upon boiling with dilute sulphuric acid, and on bringing into a vessel from which hydrogen is evolved by the action of zinc and dilute sulphuric acid, is described, § 230.

2. Anhydrous PHOSPHORIC ACID is a white, snowlike mass, which rapidly deliquesces in the air, and dissolves in water with a hissing noise. It forms with water and bases, three different series of compounds: viz., with three equivalents of water or base, hydrate of common phosphoric acid or common phosphates (tribasic); with two equivalents of water or base, hydrate of pyrophosphoric acid or pyrophosphates (bibasic); with one equivalent of water or base, hydrate of metaphosphoric acid or metaphosphates (monobasic).

The PHOSPHATES which we generally meet with in nature and in analytical investigations belong, as a rule, to the tribasic series; we therefore make them alone the object of a fuller study in this place, devoting a supplemental paragraph to a briefer consideration of monobasic and bibasic phosphoric acids, and their salts.

3. The HYDRATE OF TRIBASIC PHOSPHORIC ACID ($3\ H\ O, P\ O_5$) forms colorless and pellucid crystals, which deliquesce rapidly in the air to a syrupy non-caustic liquid. The action of heat changes it into hydrated pyro- or metaphosphoric acid, according as either one or two equivalents of water are expelled. Heated in an open platinum dish, the hydrate of common phosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes.

4. The action of heat fails to decompose the TRIBASIC PHOSPHATES with fixed bases, but converts them into pyrophosphates, if they contain one equivalent of basic water or ammonia, and into metaphosphates, if they contain two equivalents. The tribasic phosphates with alkaline base alone are soluble in water, in the neutral state. The solutions manifest an alkaline reaction. If pyro- or metaphosphates are fused with carbonate of soda, the fused mass contains the phosphoric acid invariably in the tribasic state.

5. *Chloride of barium* produces in aqueous solutions of the neutral or basic phosphates, but not in solution of the hydrate, a white precipitate of PHOSPHATE OF BARYTA $2\ Ba\ O, H\ O, P\ O_5$; or $3\ Ba\ O, P\ O_5$,* which is soluble in hydrochloric acid and in nitric acid, but difficultly soluble in chloride of ammonium.

6. *Solution of sulphate of lime* produces in neutral or alkaline solutions of phosphates, but not in solutions of the hydrate, a white precipitate of PHOSPHATE OF LIME ($2\ Ca\ O, H\ O, P\ O_5$ or $3\ Ca\ O,$

* Precipitates of the former composition are produced in solutions containing an alkaline phosphate with two equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate with three equivalents of a fixed base or ammonia.

$P O_5$) which dissolves readily in acids, even in acetic acid, and to some extent in chloride of ammonium.

7. *Sulphate of magnesia* produces in concentrated solutions of neutral phosphates a white precipitate of PHOSPHATE OF MAGNESIA ($2 Mg O, H O, P O_5 + 14$ aq.), which often separates only after some time; upon boiling, however, a precipitate of basic salt ($3 Mg O, P O_5 + 5$ aq.) is thrown down immediately. The latter precipitate forms also upon addition of sulphate of magnesia to the solution of a basic alkaline phosphate. But if *sulphate of magnesia*, mixed with a sufficient quantity of chloride of ammonium to leave the solution clear upon addition of ammonia,* is added to a solution of free phosphoric acid or of an alkaline phosphate, and ammonia in excess is then added, a white, crystalline, and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2 Mg O, N H_4 O, P O_5 + 12$ aq.) is formed, even in highly dilute solutions. This precipitate is insoluble in ammonia and most sparingly soluble in chloride of ammonium, but dissolves readily in acids, even in acetic acid. It makes its appearance often only after the lapse of some time; stirring promotes its separation (see § 101, 7). This reaction is only decisive in absence of arsenic acid (§ 136, 9).

8. *Nitrate of silver* throws down from solutions of neutral and basic alkaline phosphates a light-yellow precipitate of PHOSPHATE OF SILVER ($3 Ag O, P O_5$), which is readily soluble in nitric acid and in ammonia. If the solution contained a basic phosphate, the fluid in which the precipitate is suspended manifests a neutral reaction; whilst the reaction is acid if the solution contained a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the 3 equivalents of oxide of silver which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water; and as the latter does not neutralize the acid properties of the nitric acid, the solution becomes acid.

9. If to a solution containing phosphoric acid and the *least possible excess* of hydrochloric or nitric acid, a tolerably large amount of acetate of soda is added, and then a drop of *sesquichloride of iron*, a yellowish-white, flocculent-gelatinous precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON ($Fe_2 O_3, P O_5 + 4$ aq.) is formed. An excess of sesquichloride of iron must be avoided, as acetate of sesquioxide of iron (of red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; but only in absence of arsenic acid, which exhibits the same behavior towards sesquichloride of iron. To effect the complete separation of the phosphoric acid from the alkaline earths,

* [See § 136, 9.]

a sufficient quantity of sesquichloride of iron is added to impart a reddish color to the solution, which is then boiled (whereby the whole of the sesquioxide of iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If you wish to detect, by means of this reaction, phosphoric acid in presence of a large proportion of sesquioxide of iron, boil the hydrochloric acid solution with sulphite of soda until the sesquichloride is reduced to protochloride, which reduction is indicated by the decoloration of the solution; add carbonate of soda until the fluid is nearly neutral, then acetate of soda, and finally one drop of sesquichloride of iron. The reason for this proceeding is, that acetate of protoxide of iron does not dissolve phosphate of sesquioxide of iron.

10. When 2 or 3 drops of a neutral or acid solution containing phosphoric acid, are poured into a test tube filled to the depth of ½ to 1 inch with solution of *molybdate of ammonia* in nitric acid (§ 53), there is formed in the cold, either immediately or after the lapse of a short time, unless the solution under examination contains only a very minute amount of phosphoric acid, a pulverulent pale-yellow precipitate, which gathers upon the sides and bottom of the tube. If the precipitate does not appear within a few minutes, the operator may add cautiously and by degrees, more of the substance to be tested. Only when the phosphoric acid is present in exceedingly minute quantity, e. g., 0.00002 grm., is it requisite to wait some hours and to apply a gentle heat, not to exceed 100° Fahr., before the precipitate appears. When other coloring matters are not present, the liquid above the precipitate is colorless. It is indispensable not to add too much of the solution to be tested for phosphoric acid, as the yellow precipitate is soluble in phosphoric and other acids (and therefore is not formed) unless a considerable excess of the molybdic solution be present. A yellow coloration of the liquid is not to be regarded as proof of the presence of phosphoric acid.

The yellow precipitate (often termed phospho-molybdate of ammonia) contains MOLYBDIC ACID, AMMONIA, WATER, and a small amount (about 3 *per cent.*) of PHOSPHORIC ACID. Its formation is prevented not only by excess of phosphoric acid, but likewise by certain organic substances, e. g. tartaric acid.* The precipitate is easily recognized even in dark-colored liquids, by giving it time to settle. If it be washed with the same molybdic solution employed in producing it (in which it is totally insoluble) and be then dissolved in ammonia, addition of a mixture of chloride of ammonium, sulphate of magnesia and ammonia to the solution will throw down phosphate of ammonia-magnesia.

* [This is probably a mistake as regards tartaric acid.]

By operating in the manner above described, there is no danger of mistaking any other substance for phosphoric acid; because, arsenic acid gives *in the cold*, no precipitate with the molybdic solution, though a yellow precipitate is formed on heating and especially on boiling (the liquid above the arsenical precipitate has a yellow color), and silicic acid does not react at all in the cold, though on heating it causes a strong yellow coloration, but gives no precipitate.

11. If a finely powdered substance containing phosphoric acid (or also a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of carbonate of soda, 1 part of nitrate of potassa, and 1 part of silicic acid, the mixture fused in a platinum spoon or crucible, the fused mass boiled with water, the solution obtained decanted, carbonate of ammonia added to it, the fluid boiled again, and the silicic acid which is thereby precipitated filtered off, the filtrate now holds in solution alkaline phosphate, and may accordingly be tested for phosphoric acid as directed in 7, 8, 9, or 10.

12. *White of egg* is not precipitated by solution of hydrate of tribasic phosphoric acid, nor by solutions of tribasic phosphates, mixed with acetic acid.

§ 146.

Supplement.

a. Bibasic phosphoric acid. The solution of the hydrate 2 H O, P O_5 is converted by boiling into solution of the hydrate 3 H O, P O_5. The solutions of the salts bear heating without suffering decomposition; but upon boiling with a strong acid, the phosphoric acid is converted into the tribasic state. If the salts are fused with carbonate of soda in excess, tribasic phosphates are produced. Of the neutral pyrophosphates only those with alkaline bases are soluble in water; the acid salts (*e. g.*, Na O, H O, P O_5) are by ignition converted into metaphosphates (Na O, P O_5). *Chloride of barium* fails to precipitate the free acid; from solutions of the salts it precipitates PYROPHOSPHATE OF BARYTA (2 Ba O, P O_5). *Nitrate of silver* throws down from a solution of the hydrate, especially upon addition of an alkali, a white, earthy-looking precipitate of PYROPHOSPHATE OF SILVER (2 Ag O, P O_5), which is soluble in nitric acid and in ammonia. *Sulphate of magnesia* precipitates PYROPHOSPHATE OF MAGNESIA (2 Mg O, P O_5). The precipitate dissolves in an excess of the phosphate, as well as in an excess of the sulphate of magnesia. Ammonia fails to precipitate it from these solutions. Upon boiling the solution, it separates again. *White of egg* is not precipitated by solution of the hydrate, nor by solutions of the salts, mixed with acetic acid. *Molybdate of ammonia*, with addition of nitric acid, fails to produce a precipitate.

β. Monobasic phosphoric acid. Five sorts of monobasic phosphates are known, and the hydrates also of most of these have been produced. The several reactions by which to distinguish between these I will not enter upon here, and confine myself to the simple observation that the monobasic phosphoric acids differ from the bibasic and tribasic phosphoric acids in this, that the solutions of the hydrates of the monobasic acids precipitate *white of egg* at once, and the solutions of their salts, after addition of acetic acid. Those hydrates and salts which are precipitated by *nitrate of silver* produce with that reagent a white precipitate. A mixture of *sulphate*

of magnesia, chloride of ammonium, and ammonia fails to precipitate the monobasic phosphoric acids and their salts, or produces precipitates soluble in chloride of ammonium. All monobasic phosphates yield upon fusion with carbonate of soda tribasic phosphate of soda.

§ 147.

b. Boracic Acid ($B O_3$).

1. Boracic acid, in the anhydrous state, is a colorless, fixed glass, fusible at a red heat; hydrate of boracic acid ($H O, B O_3$) is a porous, white mass; in the crystalline state ($H O, B O_3 + 2$ aq.), it presents small scaly laminæ. It is soluble in water and in spirit of wine; upon evaporating the solutions, a large proportion of boracic acid volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus-paper, and impart to turmeric paper a faint red tint, which acquires intensity upon drying. The borates are not decomposed upon ignition; those with alkaline bases alone are readily soluble in water. The solutions are colorless, and all of them, even those of the acid salts, manifest alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, if not too highly dilute, a white precipitate of borate of baryta, which is soluble in acids and ammoniacal salts. The formula of this precipitate, when thrown down from solutions of neutral borates, is $Ba O, B O_3$ + aq.; when thrown down from solutions of acid borates, $3 Ba O, 5 B O_3 + 6$ aq. (*H. Rose.*)

3. *Nitrate of silver* produces in concentrated solutions of neutral borates of the alkalies a white precipitate, inclining slightly to yellow from admixture of free oxide of silver ($Ag O, B O_3 + H O$); in concentrated solutions of acid borates, a white precipitate of $3 Ag O, 4 B O_3$. Dilute solutions of borates give with nitrate of silver a grayish-brown precipitate of oxide of silver (*H. Rose*). All these precipitates dissolve in nitric acid and in ammonia.

4. If dilute *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot prepared solutions of alkaline borates, the boracic acid separates upon cooling, in the form of shining crystalline scales.

5. If alcohol is poured over free boracic acid or a borate—with addition, in the latter case, of *a sufficient quantity of concentrated sulphuric acid* to liberate the boracic acid—and the alcohol is kindled, the flame appears of a very distinct yellowish-green color, especially upon stirring the mixture; this tint is imparted to the flame by the ignited boracic acid which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the first flickering of the flame its borders will now appear green, even though the quantity of the boracic acid be so minute that it fails

to produce a perceptible coloring of the flame, when treated in the usual manner. THE SULPHURIC ACID EMPLOYED MUST BE CONCENTRATED, AND MUST BE ADDED IN CONSIDERABLE QUANTITY. As salts of copper also impart a green tint to the flame of alcohol, the copper which might be present must first be removed by means of hydrosulphuric acid. Presence of metallic chlorides also may lead to mistakes, as the chloride of ethyle formed in that case colors the borders of the flame greenish.

6. If the solution of boracic acid or of an alkaline or earthy borate is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of *turmeric paper* is half dipped into it, and then dried on a watch-glass at 112° Fah., the dipped half shows a peculiar RED tint (*H. Rose*).

This reaction is very delicate; care must be taken not to confound the characteristic red coloration with the blackish-brown color which turmeric paper acquires when moistened with rather concentrated hydrochloric acid, and then dried or with the brownish-red occasioned by sesquichloride of iron or by acid solutions of molybdic acid [or the orange-red produced by acid solutions of zirconia.]

When turmeric paper that has been reddened by boracic acid is moistened with solution of an alkali or alkaline carbonate, its color passes into bluish or greenish-black. Hydrochloric acid restores the red tint. (*A. Vogel, H. Ludwig.*)

7 If a substance containing boracic acid is reduced to a fine powder, this, with addition of a drop of water, mixed with 3 times its weight of a flux composed of 4½ parts of bisulphate of potassa and 1 part of finely pulverized fluoride of calcium, free from boracic acid, and the paste exposed on the loop of a platinum wire to the inner flame of the blowpipe, fluoride of boron escapes, which imparts to the flame—though only for a few instants—a yellow-green tint. This reaction may be produced with easily decomposable substances by moistening them with hydrofluosilicic acid and then bringing into the flame.

§ 148.

c. OXALIC ACID ($C_4O_6 = \bar{O}$).

1. The HYDRATE OF OXALIC ACID ($2\,H\,O, C_4\,O_6$) is a white powder; the crystallized acid ($2\,H\,O, C_4\,O_6 + 4$ aq.) forms colorless rhombic prisms. Both dissolve readily in water and in spirit of wine. When heated rapidly in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating and provoke coughing. If the hydrate is heated in a test-tube, the greater part of it sublimes unaltered.

2. All the OXALATES undergo decomposition at a red heat, the oxalic acid being converted into carbonic acid and carbonic oxide. Those with an alkali or an alkaline earth for base are in this process converted into carbonates (if pure, almost without separation of charcoal); oxalate of magnesia yields pure magnesia on gentle ignition; those with a metallic base leave either the pure metal or the oxide behind, according to the greater or less degree of reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. *Chloride of barium* produces in neutral solutions of oxalates a white precipitate of OXALATE OF BARYTA ($2\,Ba\,O, C_4\,O_6 + 2$ Aq.), which is very slightly soluble in water, more largely in acetic or oxalic acid, and in solution of chloride of ammonium, easily in nitric acid and in hydrochloric acid. From solution in the last named acids it is reprecipitated by ammonia unaltered.

4. *Nitrate of silver* produces in aqueous solutions of oxalic acid and alkaline oxalates a white precipitate of OXALATE OF SILVER ($2\,Ag\,O, C_4\,O_6$), which is almost insoluble in water, difficultly soluble in dilute nitric acid, easily soluble in hot strong nitric acid and in ammonia.

5. *Lime-water* and all the *soluble salts of lime*, and consequently also *solution of sulphate of lime*, produce in even highly dilute solutions of free oxalic acid or of oxalates, white, finely pulverulent precipitates of OXALATE OF LIME ($2\,Ca\,O, C_4\,O_6 + 2$ aq. and sometimes $2\,Ca\,O, C_4\,O_6 + 6$ aq.) which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid, and almost totally insoluble in water. The presence of salts of ammonia does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of the free oxalic acid by salts of lime. In *highly dilute* solutions the precipitate is only formed after some time.

6. If hydrated oxalic acid (or an oxalate), in the dry state, is heated with an excess of *concentrated sulphuric acid*, the latter withdraws from the oxalic acid its constitutional water, and thus causes its decomposition into CARBONIC ACID and CARBONIC OXIDE ($C_4\,O_6 = 2\,CO + 2\,CO_2$), the two gases escaping with effervescence. If the quantity operated upon is not too minute, the escaping carbonic oxide gas may be kindled; it burns with a blue flame. Should the sulphuric acid acquire a dark color in this reaction, this is a proof that the oxalic acid contained some organic substance in admixture.

7. If oxalic acid or an oxalate is mixed with some finely pulverized *binoxide of manganese* (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence ensues, caused by the escaping carbonic acid: $2\,Mn\,O_2 + C_4\,O + 2\,SO_3 = 2\,(Mn\,O\,SO_3) + 4\,CO_2$.

8. If oxalates of the alkaline earths are boiled with a concentra-

ted solution of *carbonate of soda*, and the fluid filtered, the oxalic acid is obtained in the filtrate in combination with soda, whilst the precipitate contains the base as carbonate. Some oxalates of the heavy metals, e. g., oxalate of nickel, are not entirely decomposed in this manner, soluble double oxalates being formed. Sulphide of ammonium or hydrosulphuric acid must, therefore, be employed to separate these bases.

§ 149.

d. Hydrofluoric Acid (H F).

1. Anhydrous Hydrofluoric acid is a colorless, corrosive gas, which fumes when exposed to the air, and is freely absorbed by water. Aqueous hydrofluoric acid is distinguished from all other acids by the exclusive property it possesses of dissolving crystallized silicic acid, and also the silicates which are insoluble in hydrochloric acid. Fluoride of silicon and water are formed in the process of solution ($2\,H\,F + Si\,O_2 = Si\,F_2 + 2\,H\,O$). Hydrofluoric acid decomposes with metallic oxides in the same manner, metallic fluorides and water being formed.

2. The fluorides of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkaline earths are either altogether insoluble in water, or they dissolve in that menstruum only with very great difficulty. Fluoride of aluminum is readily soluble. Most of the fluorides corresponding to the oxides of the heavy metals are very difficultly soluble in water, for instance, fluorides of copper, lead, and zinc; many other of the fluorides of the heavy metals dissolve in water without difficulty, as, for instance, the sesquifluoride of iron, protofluoride of tin, fluoride of mercury, &c. Many of the fluorides insoluble or difficultly soluble in water dissolve in free hydrofluoric acid, others do not. Most of the fluorides bear ignition in a crucible without suffering decomposition.

3. *Chloride of barium* precipitates free hydrofluoric acid imperfectly, more completely the solutions of alkaline fluorides; the voluminous white precipitate of Fluoride of Barium (Ba F) is quite insoluble in water, but dissolves in a large excess of hydrochloric or nitric acid. From these solutions it is thrown down incompletely or not at all by ammonia, being somewhat soluble in ammonia salts.

4. *Chloride of calcium* produces in aqueous solutions of hydrofluoric acid or of fluorides a gelatinous precipitate of fluoride of calcium (Ca F), which is so transparent, as at first to induce the belief that the fluid has remained perfectly clear. Addition of ammonia promotes the complete separation of the precipitate. The precipitated fluoride of calcium is insoluble in water, is very slightly soluble in hydrochloric acid and nitric acid in the cold; it dissolves somewhat more largely upon boiling with hydrochloric

acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the salt of ammonia formed retains it in solution. It is scarcely more soluble in free hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, no matter whether soluble or insoluble, is treated in a platinum crucible with just enough *concentrated sulphuric acid* to make a thin paste, the crucible covered with the convex face of a watch-glass of hard glass coated with bees-wax,* which has been removed again in some places by tracing lines in it with a pointed bit of wood, the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found ETCHED into the glass. If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This reappearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess.

The appearance of lines, after breathing on the glass, is not necessarily evidence of the presence of hydrofluoric acid in the substance under examination, unless they can be reproduced after the glass has been rinsed, dried and wiped, though their non-appearance is proof of its absence.

This reaction (5) fails if there is too much silicic acid present, or if the body under examination is not decomposed by sulphuric acid. In such cases the one or the other of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride *decomposable by sulphuric acid*, but mixed with a large proportion of silicic acid, the fluorine in it may be detected by heating the mixture in a test-tube with *concentrated sulphuric acid*, as FLUOSILICIC GAS is evolved in this process, which forms dense white fumes in moist air. If the gas is conducted into water, through a bent tube moistened inside, the latter has its transparency more or less impaired, by the separation of silicic acid. If the quantity operated upon is rather considerable, hydrate of silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid.

* The coating with wax may be readily effected by heating the glass cautiously, and putting a small piece of wax upon the convex face, and spreading the fused mass equally over it. The removal of the wax coating is effected by heating the glass gently, and wiping the wax off with a cloth.

† The statement of *Nickles*, that sulphuric acid and all acids adapted to decompose fluorides, etch glass, I have not been able to confirm when employing Bohemian glass. It is, however, advisable to prove by trial that the sulphuric acid one uses really does not attack the glass.

The following process answers best for the detection of smaller quantities of fluorine. The substance is heated with concentrated sulphuric acid in a flask closed by a perforated cork bearing two tubes. Through one tube which should reach nearly to the bottom of the flask, is passed a slow current of dried air which finds exit through the other short tube, and is made then to stream through some ammonia contained in a U tube by attaching the latter to an aspirator. The fluoride of silicon carried over by the stream of air, is decomposed on reaching the ammonia, especially when the latter is heated, fluoride of ammonium and hydrated silica being formed. The liquid is filtered, the filtrate is evaporated to dryness in a platinum crucible and the residue tested according to 5.

In the case of more difficultly decomposable substances bisulphate of potassa is used instead of sulphuric acid, and the mixture, to which some marble is likewise added, heated to fusion, and kept in that state for some time.

7. Compounds not decomposable by sulphuric acid must first be fused with four parts of carbonate of soda and potassa. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel, hydrochloric acid added to feebly acid reaction, and the fluid allowed to stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 5. (*H. Rose.*)

8. Minute quantities of metallic fluorides in minerals, slags, &c., may also be readily detected by means of the *blowpipe*. To this end, bend a piece of platinum foil, gutter-shape, then insert it in a glass tube as shown in Fig. 29, introduce the finely triturated substance mixed with powdered phosphate of soda and ammonia fused on charcoal, and let the blowpipe flame play upon it in a manner to make the products of combustion pass into the tube. If fluorides of metals are present, hydrofluoric acid gas is evolved, which betrays its presence by its pungent odor, the dimming of the glass tube, and the yellow tint which the acid air issuing from the tube imparts to a moist slip of Brazil-wood paper* (*Berzelius, Smithson*). When silicates containing metallic fluorides are treated in this manner, gaseous fluoride of silicon is formed, which also colors yellow a moist slip

Fig. 29.

* Prepared by moistening slips of fine printing-paper with decoction of Brazil wood.

of Brazil-wood paper inserted in the tube, and leads to silicic acid being deposited within the tube. After washing and drying the tube, the latter appears here and there dimmed. In the case of minerals containing water, presence of even a small proportion of metallic fluorides will, upon heating, even without addition of phosphate of soda and ammonia, usually suffice to color yellow a moistened slip of Brazil-wood paper inserted in the tube (*Berzelius*).

§ 150.

Recapitulation and remarks.—The baryta compounds of the acids of the third division are dissolved by hydrochloric acid, apparently without undergoing decomposition; alkalies therefore reprecipitate them unaltered, by neutralizing the hydrochloric acid. The baryta compounds of chromic, sulphurous, hyposulphurous, and iodic acids show, however, the same deportment; these acids must, therefore, if present, be removed before any conclusion regarding the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a salt of baryta by alkalies. But even leaving this point altogether out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less still as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions the salts of baryta in question, and more particularly the borate of baryta and the fluoride of barium, if the solution contains any considerable proportion of free acid or of an ammoniacal salt. *Boracic acid* may be invariably detected by the characteristic tint which it communicates to the flame of alcohol, as well as by its reaction with turmeric paper. The latter reaction is particularly adapted to detect minute quantities. Care should be taken to concentrate the solution sufficiently before testing. Solutions of free boracic acid must be combined with an alkali before evaporating, otherwise a large portion of the acid will volatilize along with the aqueous vapors. Metallic oxides, if present, should be removed, which may be done by hydrosulphuric acid or sulphide of ammonium.

The detection of *phosphoric acid* in compounds soluble in water is not difficult; the reaction with sulphate of magnesia is the best adapted to effect the purpose. To compounds which are insoluble in water, sulphate of magnesia cannot be applied. In phosphates of the alkaline earths, phosphoric acid may be detected and separated by means of sesquichloride of iron (§ 145, 9). In presence of alumina and sesquioxide of iron, solution of molybdate of ammonia in nitric acid is best employed. Both reagents must be used strictly according to the directions already given (§ 145, 9 and 10),

if satisfactory results are looked for. Phosphates of the oxides of groups 4, 5, or 6, may be treated either as described, § 145, 11 or, the base being thrown down by hydrosulphuric acid or sulphide of ammonium, the acid may be looked for in the filtrate.

Oxalic acid may always be easily detected in aqueous solutions of alkaline oxalates by solution of sulphate of lime. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt, the oxalate of lime may be readily distinguished from the paratartrate, or racemate, by simple ignition, with exclusion of the air, as the decomposed paratartrate leaves a considerable proportion of charcoal behind; the paratartrate dissolves moreover in cold solution of potassa or soda, in which oxalate of lime is insoluble. The deportment of the oxalates with sulphuric acid, or with binoxide of manganese and sulphuric acid, affords also sufficient means to confirm the results of other tests. In insoluble salts the oxalic acid is detected most safely by decomposing the insoluble compound by boiling with solution of carbonate of soda, by hydrosulphuric acid or sulphide of ammonium, according to circumstances. (See § 148, 8). I must finally call attention here to the fact that there are certain soluble oxalates which are not precipitated by salts of lime; these are more particularly oxalate of sesquioxide of chromium, and oxalate of sesquioxide of iron. Their non-precipitation is owing to the circumstance that these salts form soluble double salts with oxalate of lime. In salts decomposable by sulphuric acid, the *hydrofluoric acid* is readily detected; only, it must be borne in mind that too much sulphuric acid hinders the free escape of hydrofluoric acid gas, and thus impairs the delicacy of the reaction, and that the glass cannot be distinctly etched, if, instead of hydrofluoric gas, fluosilicic gas alone is evolved. Therefore, in the case of compounds abounding in silica, the safer way is to try, besides the reaction given § 149, 5, also the one given in § 149, 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given § 149, 7.

§ 151.

PHOSPHOROUS ACID ($P O_3$), when anhydrous, is a white powder which may be sublimed in close vessels but burns if heated in contact with the air. In combination with water it forms a syrupy liquid. On long standing it crystallizes, when heated it decomposes into hydrated phosphoric acid and non-spontaneously inflammable phosphoretted hydrogen gas: It is easily soluble in water. Its salts with alkaline bases are readily soluble in water, the other phosphites are with difficulty dissolved by water, but easily by dilute acids. On ignition, the phosphites are converted into phosphates, hydrogen gas or a mixture of hydrogen and phosphoretted hydrogen being evolved. With *nitrate of silver*, especially on addition of ammonia

and warming, they cause reduction and separation of metallic silver; with *nitrate of protoxide of mercury*, under similar circumstances, separation of metallic mercury. From solution of *chloride of mercury* in excess, phosphorous acid, after some time, more speedily on heating, throws down subchloride of mercury. *Chloride of barium* and *chloride of calcium* with addition of ammonia, yield in moderately dilute solutions, white precipitates which are soluble in acetic acid. A mixture of *sulphate of magnesia*, chloride of ammonium and ammonia precipitates only somewhat concentrated solutions. *Acetate of lead* throws down white phosphite of lead which is insoluble in acetic acid. When phosphorous acid is heated to boiling with excess of *sulphurous acid*, sulphur separates and phosphoric acid is produced. Phosphorous acid when placed in contact with *zinc* and *dilute sulphuric acid*, evolves a mixture of hydrogen and phosphoretted hydrogen which smokes in the air, burns with an emerald green flame and throws down phosphide of silver from a solution of nitrate of silver.

Fourth Division of the First Group of Inorganic Acids.

§ 152.

a. Carbonic Acid ($C O_2$).

1. Carbon is a solid, tasteless, and inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization (*Silliman, Despretz*). Carbon is combustible, and yields carbonic acid when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond the carbon is crystallized, transparent, exceedingly hard, difficultly combustible; in the form of graphite, it is opaque, blackish-gray, soft, greasy to the touch, difficultly combustible, and stains the fingers; as charcoal, produced by the decomposition (destructive distillation) of organic matters, it is black, opaque, noncrystalline—often dense, shining, difficultly combustible—often porous, dull, readily combustible.

2. Carbonic acid, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another. It is almost inodorous, has a sourish taste, and reddens moist litmus-paper; but the red tint disappears again upon drying. Carbonic acid is readily absorbed by solution of potassa; it dissolves pretty copiously in water.

3. The aqueous solution of carbonic acid has a feebly acid, pungent taste; it transiently imparts a red tint to litmus-paper, and colors solution of litmus wine-red; it loses its carbonic acid upon the application of heat, and also when shaken with air in a half-filled bottle. Many of the carbonates lose their carbonic acid upon ignition; those with colorless oxides are white or colorless. Of the neutral [illegible] those with alkaline bases are soluble in water. [illegible] fest a very strong alkaline reaction. Besides th[illegible] alkaline bases, those also with an alkaline ear[illegible] some of those with a metallic base, dissolve as aci[illegible].

4. The carbonates are decomposed by all *free acids* soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. The decomposition of the carbonates by acids is attended with EFFERVESCENCE, the carbonic acid being disengaged as a colorless and almost inodorous gas, which transiently imparts a reddish tint to litmus-paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence, if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid by this method, should first be heated with a little water, to prevent any mistake which might arise from the escape of air-bubbles upon treating the dry substances with the acid. Lime-water may be substituted for pure water if it is feared that carbonic acid will escape on boiling. If it is wished to determine by a direct experiment whether the disengaged gas is really carbonic acid or not, this may be readily accomplished by dipping the end of a glass rod in baryta-water, and inserting the rod into the test-tube, bringing the moistened end near the surface of the fluid in the tube, when ensuing turbidity of the baryta-water on the glass rod will prove that the evolved gas is really carbonic acid, since

5. *Lime-water* and *baryta-water*, when brought into contact with carbonic acid or with soluble carbonates, produce white precipitates of neutral CARBONATE OF LIME (CaO, CO_2), or neutral CARBONATE OF BARYTA (BaO, CO_2). When testing for free carbonic acid, the reagents ought always to be added in excess, as the *acid* carbonates of the alkaline earths are soluble in water. The precipitated carbonates of lime and baryta dissolve in acids, with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition.

Since a minute quantity of carbonate of lime is taken up by lime-water, the latter should be saturated with carbonate of lime by continued digestion with it for some time before being employed for detecting very small traces of carbonic acid.—(*Welter*, *Berthollet*.)

6. *Chloride of calcium* and *chloride of barium* immediately produce in solutions of neutral alkaline carbonates, precipitates of CARBONATE OF LIME or of CARBONATE OF BARYTA; in dilute solutions of bicarbonates these precipitates are formed only upon ebullition; with free carbonic acid these reagents give no precipitate.

§ 153.

b. SILICIC ACID.

1. SILICIC ACID is colorless or white, even ... est blowpipe flame unalterable and infusible. It fuses ... of the oxyhy-

drogen blowpipe. It is met with in two modifications (more correctly speaking, in the crystalline and in the amorphous state). It is insoluble in water and acids, with the exception of hydrofluoric acid; whilst its hydrate is soluble in acids, but only at the moment of its separation. The amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of caustic alkalies and of fixed alkaline carbonates; but the crystallized acid is insoluble or nearly so in these fluids. If either of the two is fused with pure alkalies or alkaline carbonates, a basic silicate of the alkali is obtained, which is soluble in water. The SILICATES with alkaline bases alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids*. If a large proportion of hydrochloric acid is added at once to even concentrated solutions of alkaline silicates, the separated silicic acid remains in solution; but if the hydrochloric acid is added gradually drop by drop, whilst stirring the fluid, the greater part of the silicic acid separates as gelatinous hydrate. The more dilute the fluid, the more silicic acid remains in solution, and in *highly* dilute solutions no precipitate is formed. But if the solution of an alkaline silicate, mixed with hydrochloric or nitric acid in excess, is evaporated to dryness, silicic acid separates in proportion as the acid escapes; upon treating the residue with hydrochloric acid and water, the silicic acid remains in the free state (or, if the temperature in the process of drying was restricted to 212°, as hydrate, H O, 4 Si O$_2$), as an insoluble white powder. Chloride of ammonium produces in moderately dilute solutions of alkaline silicates precipitates of hydrate of silicic acid containing alkali. The separation is facilitated by warming.

3. Part of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, part of them are not affected by these acids, not even upon boiling. In the decomposition of the former, the greater portion of the silicic acid separates usually as gelatinous, more rarely as pulverulent hydrate. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated hydrate of silicic acid suspended in it, is evaporated to dryness, the residue heated at a temperature somewhat above the boiling point of water until no more acid fumes escape, then moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary insoluble silicic acid.

4. Of the silicates not decomposed by hydrochloric acid, many, *e. g.*, kaolin, are completely decomposed by heating with a mixture of 8 parts of hydrated sulphuric acid and three parts of water, the decomposition being attended with separation of silicic acid in the pulverulent form; many others are acted upon to some extent by this reagent.

5. If any silicate, reduced to a fine powder, is fused with 4 parts of *carbonate of potassa and soda* until the evolution of carbonic acid has ceased, and the fused mass is then boiled with water, the greater portion of the silicic acid dissolves as alkaline silicate, whilst the alkaline earths, the earths proper (with the exception of alumina and glucina, which are more or less perfectly dissolved), and the heavy metallic oxides are left behind. If the fused mass is treated with water, then, without previous filtration, hydrochloric or nitric acid added to strongly acid reaction, and the fluid evaporated to dryness as directed in 3, the silicic acid is left undissolved, whilst the bases are dissolved. If the powdered silicate is fused with 4 parts of *hydrate of baryta*, the fused mass digested with water, with addition of hydrochloric or nitric acid, and the acid solution evaporated to dryness as directed in 3, the silicic acid separates, and the bases, especially the alkalies, are found in the filtrate.

[6. If an insoluble alkaline silicate is mixed in the state of powder with 3 times its weight of precipitated *carbonate of lime* and one-half its weight of *chloride of ammonium* in powder, and the mixture is heated in a platinum crucible in a slow charcoal fire for half an hour, too high a heat being avoided, a somewhat sintered mass is obtained, which, on being digested in hot water, falls to powder, and yields a solution containing, besides chloride of calcium and hydrate of lime, all, or nearly all the alkalies of the silicate, in the form of chlorides.—(*J. Lawrence Smith.*)]

7. When *hydrofluoric acid*, in concentrated aqueous solution or as gas, is allowed to act on silicic acid, gaseous fluoride of silicon is formed ($Si O_2 + 2 H F = Si F_2 + 2 H O$): dilute hydrofluoric acid dissolves silica to hydrofluosilicic acid ($Si O_2 + 3 H F = Si F_2, H F + 2 H O$). By the action of hydrofluoric acid upon silicates, silicofluorides are produced ($Ca O, Si O_2 + 3 H F = Si F_2, Ca F, + 3 H O$), which when heated with strong sulphuric acid are converted into sulphates with evolution of hydrofluoric acid and fluoride of silicon. If the powdered silicate is mixed with 5 parts of fluoride of calcium in powder, the mixture made into a paste with hydrated sulphuric acid, and heat applied (best in the open air), until no more fumes escape, the whole of the silicic acid present volatilizes as fluosilicic gas. The bases present are found in the residue as sulphates, mixed with sulphate of lime.

8. If silicic acid or a silicate is fused with *carbonate of soda* on the loop of a platinum wire, a FROTHING is observed in the fusing bead, owing to the disengagement of carbonic acid. If the proper proportion of carbonate of soda is not exceeded, the bead of silicate of soda formed in the process will remain transparent on cooling.

9. *Phosphate of soda and ammonia*, in a state of fusion, fails nearly altogether to dissolve silicic acid. If therefore silicic acid

or a silicate is heated, in small fragments, with phosphate of soda and ammonia on a platinum wire, the bases are dissolved, whilst the silicic acid separates and floats about in the clear bead, as a more or less transparent mass, exhibiting the shape of the fragment used in the experiment.

§ 154.

Recapitulation and remarks.—Free carbonic acid is readily known by its deportment with lime-water; the carbonates are easily detected by the evolution of a nearly inodorous gas, which takes place when they are treated with acids. When operating upon compounds which, besides carbonic acid, evolve other gases, the disengaged gas is to be tested with lime-water or baryta-water. Silicic acid, both in the free state and in silicates, may usually be readily detected by the reaction with phosphate of soda and ammonia. It differs, moreover, from all other bodies in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and in fusing bisulphate of potassa, and its solubility in boiling solutions of pure alkalies and alkaline carbonates. It also differs from many bodies by its completely volatilizing when repeatedly evaporated in a platinum dish with hydrofluoric acid or a mixture of fluoride of ammonium and sulphuric acid.

SECOND GROUP OF THE INORGANIC ACIDS.

ACIDS WHICH ARE PRECIPITATED BY NITRATE OF SILVER, BUT NOT BY CHLORIDE OF BARIUM: *Hydrochloric Acid*, *Hydrobromic Acid*, *Hydriodic Acid*, *Hydrocyanic Acid*, *Hydroferro-*, and *Hydroferricyanic Acid*, *Hydrosulphuric Acid*. (Nitrous acid, Hypochlorous acid, Chlorous acid, Hypophosphorous acid.)

The silver compounds corresponding to the *hydrogen acids* of this group are insoluble in dilute nitric acid. These acids decompose with metallic oxides, the metals combining with the chlorine, bromine, cyanogen, iodine, or sulphur, whilst the oxygen of the metallic oxide forms water with the hydrogen of the hydracid.

§ 155.

a. HYDROCHLORIC ACID (H Cl).

1. CHLORINE is a heavy, yellowish-green gas of a disagreeable, suffocating odor, and which has a most injurious action upon the respiratory organs; it destroys vegetable colors (litmus, indigo-blue, &c.); it is incombustible, and supports the combustion of few bodies only. Minutely-divided antimony, tin, &c., spontaneously ignite in it, being converted into chlorides. It dissolves pretty largely in water; the chlorine water formed has a faint yellowish-

green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 27), and loses its odor when shaken with mercury; in this process the latter is converted into a mixture of subchloride and metallic mercury. Small quantities of chlorine may be readily detected in a fluid, by adding the latter to a solution of pure protoxide of iron, mixed with sulphocyanide of potassium: the solution is at once colored red by the action of the free chlorine;—or, in the absence of nitrous acid, by adding the fluid to a dilute solution of iodide of potassium, mixed with starch-paste. (See § 157, 9.)

2. HYDROCHLORIC ACID, at the common temperature and common atmospheric pressure, is a colorless gas, which forms dense fumes in the air, is suffocating and very irritant, and dissolves in water with exceeding facility. The more concentrated solution (fuming hydrochloric acid) loses a large portion of its gas upon heating.

3. The neutral METALLIC CHLORIDES are readily soluble in water, with the exception of chloride of lead, chloride of silver, and subchloride of mercury; most of the chlorides are white or colorless. Many of them volatilize at a high temperature, without suffering decomposition; others are decomposed upon ignition, and many of them are fixed.

4. *Nitrate of silver* produces in even highly dilute solutions of free hydrochloric acid or of metallic chlorides white precipitates of CHLORIDE OF SILVER (Ag Cl), which upon exposure to light change first to violet, then to black; they are insoluble in nitric acid, but dissolve readily in ammonia, as well as in cyanide of potassium, and fuse without decomposition, when heated. (Compare § 118, 7).

5. *Nitrate of suboxide of mercury* and *acetate of lead* produce in solutions containing free hydrochloric acid or metallic chlorides precipitates of SUBCHLORIDE OF MERCURY (Hg_2 Cl) and CHLORIDE OF LEAD (Pb Cl). For the properties of these precipitates see § 119, 6, and § 120, 7.

6. If hydrochloric acid is heated with *binoxide of manganese*, or a chloride with *binoxide of manganese* and *sulphuric acid*, chlorine gas is evolved, which may be readily recognised by its YELLOWISH-GREEN color, its odor and its bleaching action on vegetable colors. To observe the last named effect, a slip of moistened litmus-paper is exposed to its action.

7. If a metallic chloride is triturated together with *chromate of potassa*, the mixture treated with *concentrated sulphuric acid* in a tubulated retort, and a gentle heat applied, a deep brownish-red gas is copiously evolved (CHLORO-CHROMIC ACID ($Cr O_2 Cl$), which condenses into a fluid of the same color, and passes over into the receiver. If this distillate is mixed with ammonia in excess, a yellow-colored liquid is produced; the yellow tint is imparted to

the fluid by the chromate of ammonia which forms in this process ($Cr\ O_2\ Cl + 2\ N\ H_4\ O = N\ H_4\ Cl + N\ H_4\ O,\ Cr\ O_3$); upon the addition of an acid, the color of the solution changes to a reddish yellow, owing to the formation of acid chromate of ammonia.

8. In the metallic chlorides insoluble in water and nitric acid, the chlorine is detected by fusing them with carbonate of soda and potassa, and treating the fused mass with water, which will dissolve, besides the excess of the alkaline carbonate, the chloride of the alkali metal formed in the process of fusion.

9. If in a bead of *phosphate of soda and ammonia* on a platinum wire, *oxide of copper* be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it so long as chlorine is present (*Berzelius*).

§ 156.

b. HYDROBROMIC ACID (H Br).

1. BROMINE is a heavy, reddish-brown fluid, of a very disagreeable chlorine-like odor; it boils at 116·6° F., and volatilizes rapidly even at the common temperature. The vapor of bromine is brownish-red. Bromine bleaches vegetable colors like chlorine; it is rather difficultly soluble in water, but dissolves more easily in alcohol, and very readily in ether. The solutions are yellowish-red.

2. HYDROBROMIC ACID GAS, its AQUEOUS SOLUTION and the METALLIC BROMIDES offer in their general deportment a great analogy to the corresponding chlorides.

3. *Nitrate of silver* produces in aqueous solutions of hydrobromic acid or of bromides a yellowish-white precipitate of BROMIDE OF SILVER (Ag Br), which changes to gray upon exposure to light; this precipitate is insoluble in nitric acid, and somewhat difficultly soluble in ammonia, but dissolves with facility in cyanide of potassium.

4. *Nitrate of protoxide of palladium*, but not protochloride of palladium, produces in neutral solutions of metallic bromides a reddish-brown precipitate of PROTOBROMIDE OF PALLADIUM (Pd Br). In concentrated solutions this precipitate is formed immediately, in dilute solutions it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury, upon the application of heat, and liberates the bromine, by oxidizing the hydrogen or the metal. The liberated bromine colors the solution yellow or yellowish-red. When operating upon bromides in the solid state, brownish-red (if diluted, brownish-yellow) vapors

of bromine escape, which, when evolved in sufficient quantity, condense in the cold part of the test-tube to small drops. In the cold, even red fuming nitric acid as well as solution of peroxide of nitrogen in hydrated sulphuric acid, or a mixture of hydrochloric acid and nitrite of potassa, fail to liberate the bromine contained in rather dilute solutions of metallic bromides.

6. *Chlorine*, in the *gaseous* state or in *solution*, immediately liberates bromine in the solutions of its compounds; the fluid assuming a yellowish-red tint, if the quantity of the bromine present is not too minute. A large excess of chlorine is to be avoided since it nearly or quite discharges the color by forming chloride of bromine. This reaction becomes far more sensitive by adding to the mixture some liquid which dissolves the bromine and at the same time does not mingle with the water, such as *bisulphide of carbon* or *chloroform*. The neutral or slightly acid solution of the substance under examination is placed in a test-tube, and a little of one of the above-mentioned liquids is poured in, which gathers as a globule at the bottom; dilute chlorine water is then added, drop by drop, the whole being agitated. When bromine is present in considerable quantity (*e. g.*, 1 of bromine to 1000 of water), the globule acquires a reddish-yellow color,—with very minute quantities (*e. g.*, 1 of bromine to 30,000 of water), it still has a perceptible pale-yellow tint. Ether is *far less adapted* to this test. In these experiments also, a large excess of chlorine water must be avoided, and this reagent is only applicable, if when shaken with much water and some bisulphide of carbon or chloroform it communicates no color to the latter. If the solution of bromine in bisulphide of carbon, chloroform (or ether) is mixed with some solution of potassa, and the mixture shaken, the yellow tint disappears, and the solution now contains bromide of potassium and bromate of potassa. Upon evaporation and subsequent ignition of the residue, the bromate of potassa is converted into bromide of potassium, and the ignited mass may then be further tested as directed in 7.

7. If bromides are heated with *binoxide of manganese* and *concentrated sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. Presence of large quantities of metallic chlorides is unfavorable to this reaction, and makes it necessary to add a little water, and to apply the sulphuric acid repeatedly, but in *very small* proportions, until the bromine vapors appear. If the bromine is present only in very minute quantity, the color of these vapors is not visible. The experiment should, in that case, be conducted in a small retort, and the evolved vapors transmitted through a long glass condensing tube; generally, the color will be perceptible by looking lengthwise through the tube. The first drops of the distillate will also appear yellow. These and the vapors that first go over

are conveniently received into small test-tubes, containing some starch moistened with water; since

8. If moistened *starch* is brought into contact with free bromine, especially when the latter is in the gaseous state, YELLOW BROMIDE OF STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by hermetically sealing the test-tube which contains the moistened starch and the fluid under examination, and then inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the fluid occupies the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time, will again disappear. The reaction is obtained more simply and with scarcely impaired delicacy, by warming the distillate containing bromine, or the original mixture of a bromide with binoxide of manganese, &c., in a very small beaker, which is covered with a watch-glass, to whose under side is attached a piece of paper moistened with starch-paste and sprinkled with dry starch.

9. If sulphuric acid is poured over a mixture of a bromide with *chromate of potassa*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over does not turn yellow, but becomes colorless, upon supersaturation with ammonia.

10. In the metallic bromides which are insoluble in water and nitric acid, the bromine is detected in the same way as the chlorine in the corresponding chlorides.

11. A *phosphate of soda and ammonia bead saturated with oxide of copper*, mixed with a substance containing bromine, and then ignited in the inner blowpipe flame, colors the flame BLUE, inclining to GREEN, more particularly at the edges (*Berzelius*).

§ 157.

c. HYDRIODIC ACID (H I).

1. IODINE is a solid, soft body, of a peculiar, disagreeable odor. It is generally seen in the form of black, shining, crystalline scales. It fuses at a gentle heat; at a somewhat higher temperature, it is converted into iodine vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol and ether; the aqueous solution is of a light-brown, the alcoholic and ethereal solutions are a deep red-brown color. Iodine destroys vegetable colors only slowly and imperfectly; it stains the skin brown; with starch it forms a compound of an intensely deep blue color. This compound is formed invariably when iodine vapor or a solution containing free iodine comes in contact with starch, best with

starch-paste. It is decomposed by alkalies, and also by chlorine and bromine.

2. HYDRIODIC acid gas resembles hydrochloric and hydrobromic acid gases; it dissolves copiously in water. The colorless hydrated hydriodic acid turns speedily to a reddish-brown when in contact with the air, owing to the formation of water, and a solution of iodine in hydriodic acid.

3. The IODIDES also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides, as those of lead and mercury, have characteristic colors.

4. *Nitrate of silver* produces in aqueous solutions of hydriodic acid and of iodides yellowish-white precipitates of IODIDE OF SILVER (Ag I), which blacken on exposure to light; these precipitates are insoluble in dilute nitric acid, and *very sparingly soluble in ammonia*, but dissolve readily in cyanide of potassium.

5. *Protochloride of palladium* and *nitrate of protoxide of palladium* produce even in very dilute solutions of hydriodic acid or metallic iodides a brownish-black precipitate of PROTIODIDE OF PALLADIUM (Pd I), which dissolves to a trifling extent in saline solutions (solution of chloride of sodium, chloride of magnesium, &c.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

6. A solution of 1 part of *sulphate of oxide of copper* and 2½ parts of *sulphate of protoxide of iron* throws down from neutral aqueous solutions of the iodides SUBIODIDE OF COPPER (Cu_2 I), in the form of a dirty-white precipitate. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent.

7. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic acid or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *hyponitric acid* decompose hydriodic acid and iodides with the greatest facility even in the most dilute solutions. Colorless solutions of iodides therefore acquire immediately a brownish-red color, upon addition of some red fuming nitric acid, or a mixture of this with concentrated sulphuric acid, or, better still, a solution of hyponitric acid in hydrated sulphuric acid or nitrite of potassa and some sulphuric or hydrochloric acid. From more concentrated solutions the iodine separates under these circumstances in the form of small black plates or scales, whilst nitric oxide gas and iodine vapors escape.

8. As the blue coloration of iodide of starch remains still visible in much more highly dilute solutions than the yellow color of solutions of iodine in water, the delicacy of the reaction just now de-

scribed (7) is considerably heightened by mixing the fluid to be tested for iodine first with some thin, clear *starch-paste*, then adding one or two drops of dilute sulphuric acid, to make the fluid acid, and adding finally one or the other of the reagents given in 7. Of the solution of hyponitric acid in sulphuric acid a single drop on a glass rod suffices to produce the reaction most distinctly. I can therefore strongly recommend this reagent, which was first proposed by *Otto*. Red fuming nitric acid must be added in somewhat larger quantity, to call forth the reaction in its highest intensity; this reagent therefore is not well adapted to detect *very minute* quantities of iodine. The reaction with nitrite of potassa also is of the utmost delicacy. The fluid to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of nitrite of potassa is then added. In cases where the quantity of iodine present is very minute, the fluid turns reddish instead of blue. An excess of the fluid containing nitrous acid or hyponitric acid does not materially impair the delicacy of the reaction. As iodide of starch dissolves in hot water to a colorless liquid, the fluids must of necessity be cold; the colder they are, the more delicate the reaction. When it is desired to attain the extreme limit of delicacy, the mixture is cooled with ice, the starch is allowed to settle to the bottom of the tube, and it is placed upon white paper for observing the coloration. (See also Recapitulation, § 160.)

9. *Chlorine gas* and *chlorine water* decompose compounds of iodine also, setting the iodine free; but if the chlorine is applied in excess, the liberated iodine combines with it to colorless chloride of iodine. A dilute solution of a metallic iodide, mixed with starch-paste, acquires therefore, upon addition of a little chlorine water, at once a blue tint, but becomes colorless again upon addition of more chlorine water. As it is therefore difficult not to exceed the proper limit, especially where the quantity of iodine present is only small, chlorine water is not well adapted for the detection of minute quantities of iodine.

10. If a solution in which iodine has been set free by nitrous acid (nitrite of potassa and hydrochloric acid), &c., is mixed with some *chloroform* or *bisulphide of carbon*, and the mixture shaken, leaving a few drops of the reagent undissolved, these will subside to the bottom of the fluid, exhibiting a lighter or darker red color. This reaction also is extremely sensitive. If the solution is mixed with *ether*, and the mixture shaken, the ether dissolves the liberated iodine, and acquires thereby a reddish-brown or yellow color. The color imparted to the ether by iodine is much more intense than that imparted to that fluid by an equal quantity of bromine.

11. If metallic iodides are heated with *concentrated sulphuric*

acid or with *sulphuric acid* and *binoxide of manganese*, or with *sulphuric acid* and *chromate of potassa*, iodine separates, which may be known by the color of its vapor, and, in the case of very minute quantities, also by its action upon a slip of paper coated with starch-paste.

12. The iodides which are insoluble in water and nitric acid comport themselves upon fusion with *carbonate of soda and potassa* in the same manner as the corresponding chlorides.

13. A *phosphate of soda and ammonia bead*, saturated with oxide of copper, when mixed with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN color to the flame.

§ 158.

d. HYDROCYANIC ACID (H Cy).

1. CYANOGEN is a colorless gas of a peculiar, penetrating odor; it burns with a crimson flame, and is pretty soluble in water.

2. HYDROCYANIC ACID is a colorless, volatile, inflammable liquid, the odor of which resembles that of bitter almonds; it is miscible with water in all proportions; in the pure state it speedily suffers decomposition. It is extremely poisonous.

3. The CYANIDES of the metals of the 1st and 2d groups are soluble in water; the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid; but ignition fails to decompose them, if the access of air is precluded. When fused with oxides of lead, copper, antimony, tin, &c., the cyanides reduce these oxides, and are converted into cyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed upon ignition, the cyanides of the noble metals being converted into cyanogen gas and metal, the cyanides of the other heavy metals into nitrogen gas and metallic carbides. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. By heating and evaporating with a strong sulphuric acid they are all decomposed, hydrochloric acid decomposes some of them, hydrosulphuric acid many others.

4. The cyanides have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in cyanide of potassium. The resulting compounds are either:

a. True double salts, *e. g.*, K Cy + Ni Cy. From solutions of such double salts, acids, by decomposing the cyanide of potassium, precipitate the metallic cyanide which was combined with it.—Or they are:

b. Simple haloid salts, in which a metal, *e. g.*, potassium, is combined with a compound radical consisting of cyanogen and another metal (iron, cobalt, manganese, chromium). Compounds of this

kind are the ferro- and ferricyanide of potassium, $K_2 Cy_3 Fe$ or $K_2 Cfy$, and $K_3 Cy_6 Fe_2$ or $K_3 Cfdy$, cobalticyanide of potassium, $K_3 Cy_6 Co_2$, &c. From solutions of compounds of this nature dilute acids do not separate metallic cyanides in the cold. If the potassium is replaced by hydrogen, peculiar hydracids are formed, which must not be confounded with hydrocyanic acid.

We will now first consider the reaction of hydrocyanic acid and the simple cyanides, then, in an appendix to this paragraph, those of hydroferro- and hydroferricyanic acid.

5. *Nitrate of silver* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals white precipitates of CYANIDE OF SILVER (Ag Cy), which are readily soluble in cyanide of potassium, dissolve with some difficulty in ammonia, and are insoluble in nitric acid; these precipitates are decomposed by ignition, leaving metallic silver with some paracyanide.

6. If solution of *sulphate of protoxide of iron* which has been for some time in contact with the air is added to a solution of free hydrocyanic acid, no alteration takes place; but if *solution of potassa* or *soda* is now added, a bluish-green precipitate forms, which consists of a mixture of Prussian-blue ($Fe_2 Cfy_3$), and hydrate of protosesquioxide of iron. Upon now adding hydrochloric acid (best after previous application of heat), the hydrate of protosesquioxide of iron dissolves, whilst the PRUSSIAN-BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same reactions are observed when sulphate of protoxide of iron containing sesquioxide, is added to the solution of an alkaline cyanide, with subsequent addition of hydrochloric acid.

7. If a liquid containing a small quantity of hydrochloric acid or cyanide of potassium is mixed with so much yellow sulphide of ammonium that the solution appears yellowish, and with a little ammonia, and the mixture warmed in a porcelain dish with renewal of water, if necessary, until it has become colorless, and all excess of sulphide of ammonium is destroyed or volatilized, sulphocyanide of ammonium is formed, and the fluid, after being acidified with hydrochloric acid (whereby no evolution of hydrosulphuric acid should occur), acquires a blood-red tint upon addition of sesquichloride of iron (*Liebig*). This reaction is exceedingly delicate. The following formula expresses the transformation of hydrocyanic acid into sulphocyanide of ammonium: $N H_4, S + 2 (N H_4, O) + 2 H Cy = 2 (N H, Cy S_2) + N H_4, S + 2 H O$. If an acetate [a phosphate, borate, fluoride, oxalate, or salt of an organic acid] is present, addition of more hydrochloric acid may be necessary to develope the red color.

8. Neither of the above methods will serve to effect the detection of cyanogen in cyanide of mercury. To detect cyanogen in that compound, the solution is mixed with hydrosulphuric acid: sulphide of mercury precipitates, and the solution contains free hydrocyanic acid. In solid cyanide of mercury the cyanogen is most readily detected by heating in a glass tube. Compare 3.

Appendix.

a. Hydroferrocyanic acid (H_2 Cfy). Hydroferrocyanic acid is soluble in water. Some of the ferrocyanides, as those of the alkalies and alkaline earths, are soluble in water, most of them are however insoluble. They are all decomposed by ignition. If strongly heated while containing water they yield hydrocyanic acid, carbonic acid, and ammonia; when anhydrous they give off on ignition nitrogen, and sometimes cyanogen.

In solutions of this acid or of soluble ferrocyanides, *sesquichloride of iron* produces a blue precipitate of FERROCYANIDE OF IRON (F_4 Cfy_3); *sulphate of oxide of copper*, a brownish-red precipitate of FERROCYANIDE OF COPPER (Cu_2 Cfy); *nitrate of silver*, a white precipitate of FERROCYANIDE OF SILVER (Ag_2 Cfy), which is insoluble in nitric acid and in ammonia, but dissolves in cyanide of potassium. Insoluble ferrocyanides of metals are decomposed by boiling with solution of soda, ferrocyanide of sodium being formed and the oxides thrown down unless the latter are themselves soluble in soda. When heated with 3 parts of sulphate and 1 part of nitrate of ammonia, they yield sulphates of the metals contained in them, the whole of the cyanogen volatilizing in form of cyanide of ammonium and the products of its decomposition (*Bolley*).

b. Hydroferricyanic acid. (H_3 Cfdy.) Hydroferricyanic acid and many ferricyanides are soluble in water. The ferricyanides are all decomposed at a strong heat, in a manner similar to the ferrocyanides. In the aqueous solutions of hydroferricyanic acid and its salts, *sesquichloride of iron* produces no blue precipitate, but *sulphate of protoxide of iron* produces a blue precipitate of PROTOFERRICYANIDE OF IRON (3 Fe, Cfdy); *sulphate of copper*, a yellowish-green precipitate of FERRICYANIDE OF COPPER (3 Cu, Cfdy), which is insoluble in hydrochloric acid; *nitrate of silver*, an orange-colored precipitate of FERRICYANIDE OF SILVER (3 Ag, Cfdy), which is insoluble in nitric acid, but dissolves readily in ammonia and in cyanide of potassium. The insoluble ferricyanides of metals are decomposed by boiling with solution of soda, the metallic oxides being thrown down; in the fluid filtered off from them, either ferrocyanide of sodium alone is found, or a mixture of ferro- with ferricyanide of sodium. By heating with sulphate

and nitrate of ammonia the ferricyanides are decomposed the same as the ferrocyanides.

§ 159.

e. Hydrosulphuric Acid (H S).

Sulphuretted Hydrogen.

2. Sulphur is a solid, brittle, friable, tasteless body, insoluble in water. It occurs sometimes in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish color, and sometimes in that of a yellow or yellowish-white or grayish-white powder. It melts at a moderate heat; upon the application of a stronger heat it is converted into brownish-yellow vapors, which, in cold air, condense to a yellow powder, and on the sides of the vessel, to drops. Heated in the air, it burns with bluish flame to sulphurous acid, which betrays its presence in the air at once by its suffocating odor. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of chlorate of potassa and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid; in boiling solution of soda sulphur dissolves to a yellow fluid, which contains sulphide of sodium and hyposulphite of soda; in ammonia sulphur is insoluble.

2. Hydrosulphuric acid, at the common temperature and under common atmospheric pressure, is a colorless, inflammable gas, soluble in water, and which may be readily recognised by its characteristic smell of rotten eggs; it transiently imparts a red tint to litmus paper.

3. Of the sulphides only those with alkalies and alkaline earths are soluble in water. These, and the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of hydrosulphuric acid gas, which may be readily detected by its peculiar smell, and by its action upon solution of lead (see 4). The decomposition of higher sulphides is attended also with separation of sulphur in a finely-divided state; the white precipitate may be readily distinguished from similar precipitates by its deportment on heating. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrosulphuric acid gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury, gold and platinum resist the action of both acids, but dissolve readily in nitrohydrochloric acid. Upon the solution of sulphides in nitric acid, and in nitrohydrochloric acid, sulphuric acid is formed, and the process of solution is moreover attended, in most cases, with separation of sulphur, which is readily recognised by its color and by its deportment upon heating. Many metallic sul-

to set the bromine also free, which may then be separated and identified by means of chloroform, or bisulphide of carbon. Or the liberated iodine may also be removed first by means of chloroform, or bisulphide of carbon, and the fluid then tested for bromine, by means of chlorine water and one of the just named solvents.

Metallic chlorides are detected in presence of metallic bromides by the reaction with chromate of potassa and sulphuric acid.

In conclusion may be mentioned that besides the reagents above noticed many others have been employed for liberating iodine from its combinations, *e. g.* iodic acid, or iodates of the alkalies with hydrochloric acid—(*Liebig*): sesquichloride of iron with sulphuric acid, or bichloride of platinum with hydrochloric acid—(*Hempel*): permanganate of potassa in slightly acidified solution. —(*Henry.*)

With regard to these reagents, it must be remarked that iodic acid should be employed with great caution, because, in the first place, iodine may be liberated from it by reducing agents, and because, in the second place, when used in excess, it destroys the reaction.—Sesquichloride of iron with addition of sulphuric acid does not act immediately; if time be given it the reaction ensues with the greatest delicacy, and an excess of it is not greatly injurious.—Permanganate of potassa also reacts at once, even in the dilutest solutions. Since, however, a liquid containing a trace of iodide of starch, has a reddish appearance, mistakes may arise from the color of this reagent. The reaction can therefore not be considered decisive until after the lapse of 6 to 12 hours.—It is obvious that the mode of operating may be greatly varied for the purpose of making the starch-test in the highest degree sensitive. For the particulars of such modifications as have been found useful in examinations of the utmost nicety, the operator may profitably consult the papers of *Morin** and *Hempel*.†

§ 161.

More rarely occurring Acids of the Second Group.

1. *Nitrous acid* ($N O_3$). Nitrous acid, in the free state, at the common temperature, is a brownish-red gas. In contact with water it is converted into nitric acid, which dissolves, and nitric oxide gas, which remains undissolved ($3 N O_3 = N O_5 + 2 N O_2$). The nitrites are decomposed by ignition; many of them are soluble in water. When nitrites or concentrated solutions of nitrites are treated with dilute sulphuric acid, it is not nitrous acid gas which is evolved, but nitric oxide gas attended with formation of nitric acid. In solutions of nitrites of the alkalies *nitrate of silver* produces a white precipitate, which dissolves in a very large proportion of water, especially upon application of heat; *sulphate of protoxide of iron*, upon addition of a small quantity of acid, produces a dark blackish-brown coloration, which is

* Jour. f. Prakt. Chem. 78. 1. † Ann. d. Chem. u. Pharm. 107. 102.

due to nitric oxide gas in the solution of the sulphate of protoxide of iron. *Hydrosulphuric acid* produces in neutral as well as in acid solutions copious precipitates of sulphur, attended with formation of nitrate of ammonia. Solution of *iodide of potassium*, mixed with starch paste and sulphuric acid, is, however, the most delicate test of nitrous acid. (*Price, Schönbein.*) Water which contains the one hundred-thousandth part of nitrite of potassa gives in a few seconds, and water containing but one-millionth of this salt gives in a few minutes a perceptible blue color, from the liberation of iodine and formation of iodide of starch. This reaction is only proof of the presence of nitrous acid when other substances that decompose iodide of potassium (iodic acid, sesquioxide of iron, &c.) are not present.

2. *Hypochlorous acid* (Cl O) at ordinary temperatures is a deep yellowish-green gas of an unpleasant irritating odor like that of chlorine. It is soluble in water, and the dilute aqueous solution may be distilled without decomposition. The hypochlorites usually occur combined with metallic chlorides, as in so-called chloride of lime, *Eau-de-Javelle*, &c. The solutions decompose on boiling, with formation of a chloride and a chlorate; while from concentrated solutions, oxygen is evolved. If a solution of chloride of lime is mixed with sulphuric or hydrochloric acid, chlorine is set free, while by addition of nitric acid in small quantity hypochlorous acid is liberated. *Nitrate of silver* throws down from solution of chloride of lime, chloride of silver (the hypochlorite of silver at first formed rapidly decomposing into chloride and chlorate of silver 3 (Ag O, Cl O) = Ag O, $Cl O_3$ + 2 Ag Cl): *nitrate* of lead produces at first a white precipitate which gradually becomes orange-red, and finally—from formation of binoxide of lead—brown. *Salts of protoxide of manganese* give brownish-black precipitates of hydrated binoxide. A solution of *permanganate of potassa* is not decolorized. *Litmus* and *indigo solutions* are bleached by the alkaline, more rapidly by the acidulated solutions of hypochlorites. When a solution of arsenious acid in hydrochloric acid is made blue by indigo, and poured into a solution of chloride of lime, with constant stirring, decolorization only takes place after the arsenious acid has been wholly converted into arsenic acid.

3. *Chlorous acid* ($Cl O_3$) is a yellowish-green gas of a peculiar unpleasant odor. It dissolves in water, forming even when dilute an intensely yellow liquid. The chlorites are mostly soluble in water; the solutions readily decompose into a mixture of chloride and chlorate. *Nitrate of silver* throws white chlorite of silver, which is soluble in a large amount of water; a solution of *permanganate of potassa* is at once decolorized, after some time hydrated sesquioxide of manganese separates. *Litmus* and *indigo* solutions are at once bleached even in presence of excess of arsenious acid. If the slightly acidulated dilute solution of a *protosalt of iron* is added to a dilute solution of chlorous acid, the mixture transiently acquires an amethyst color and only after some moments assumes the yellowish tinge of sesquisalts of iron. (*Lennsen.*)

4. *Hypophosphorous acid* (P O), in concentrated solution forms a syrupy liquid similar to that of phosphorous acid (§ 151), with which it agrees further by decomposing on application of heat into hydrated phosphoric acid and non-spontaneously inflammable phosphoretted hydrogen gas. The hypophosphites are all soluble in water, and on ignition are all resolved into phosphates, and in general, spontaneously inflammable phosphoretted hydrogen gas. *Chlorides of barium* and *calcium*, and *acetate of lead* give no precipitates (distinction from phosphorous acid); *nitrate of silver* yields in solutions of hypophosphites a precipitate which at first is white, but which, even at ordinary temperatures, more rapidly by heating, blackens from separation of metallic silver. Hypophosphorous acid throws down from an excess of *chloride of mercury*, slowly in the cold, rapidly on heating, a precipitate of subchloride of mercury. Brought in contact with *zinc* and *dilute sulphuric acid*, hypophosphorus acid yields hydrogen gas mixed with phosphoretted hydrogen. (Compare phosphorous acid, § 151.)

THIRD GROUP OF THE INORGANIC ACIDS.

ACIDS WHICH ARE NOT PRECIPITATED BY SALTS OF BARYTA NOR BY SALTS OF SILVER: *Nitric Acid, Chloric Acid.* (Perchloric Acid.)

§ 162.

a. NITRIC ACID (N O).

1. ANHYDROUS NITRIC ACID crystallizes in six-sided prisms. It fuses at 85·2° F., and boils at 113° F. (*Deville*). The pure hydrate is a colorless, exceedingly corrosive fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors nitrogenous matter intensely yellow. Hydrate of nitric acid containing nitrous acid has a red color.

2. All the NEUTRAL SALTS of nitric acid are soluble in water; only some of the basic nitrates are insoluble in this menstruum. All nitrates without exception undergo decomposition at an intense red heat. Those with alkaline bases yield at first oxygen, and change to nitrites, which are then further resolved into oxygen and nitrogen; the others yield oxygen and nitrous or hyponitric acid.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought into contact with a nitrate in fusion, DEFLAGRATION takes place, *i.e.*, the charcoal burns at the expense of the oxygen of the nitric acid, the combustion being attended with vivid scintillation.

4. If a mixture of a nitrate with *cyanide of potassium* in powder is heated on a platinum plate, a vivid DEFLAGRATION will ensue, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected by this reaction.

5. If a nitrate is mixed with *copper filings*, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air to nitrous acid. The coloration may be observed most distinctly by looking lengthways through the tube.

6. If the solution of a nitrate is mixed with an equal volume of concentrated sulphuric acid, free from nitric and hyponitric acid, the mixture allowed to cool, and a concentrated solution of *sulphate of protoxide of iron* then cautiously added to it so that the fluids do not mix, the stratum, where the two fluids are in immediate contact, shows a purple, afterwards a brown, or, in cases where only a very minute quantity of nitric acid is present, a reddish color. If the solutions are now mixed, a *clear*, brownish-purple liquid is obtained. In this process the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combining with the protoxide and converting a portion of it into sesquioxide,

whilst the remaining nitric oxide combines with the remaining portion of the protoxide of iron, and forms with it a peculiar compound, which dissolves in water, imparting a brownish-black color to the fluid.

A similar coloration is obtained with selenious acid; on *mixing* the solutions and allowing them to stand for some time, selenium separates as a red powder. (*Wittstock.*)

7. If some hydrochloric acid is heated to boiling in a test-tube, and one or two drops of a very dilute solution of *sulphate of indigo* are added, and the boiling continued, the liquid remains blue (if the hydrochloric acid be free from chlorine). If now there be added to the faint-blue liquid a nitrate, either solid or in solution, and the mixture be again boiled [and, if needful, evaporated to one-half or to a less volume], the liquid is decolorized by the destruction of the indigo-blue. This is a highly sensitive reaction. It must not be overlooked that some other bodies, especially free chlorine, have the same bleaching effect.

8. If a little *brucia* is dissolved in concentrated sulphuric acid, and a little of a fluid containing nitric acid added to the solution, the latter immediately acquires a magnificent red color. This reaction is exceedingly characteristic and delicate.

9. Very minute quantities of nitric acid may be detected also, by reducing, in the first place, the nitric acid to nitrous acid. This is accomplished in the wet way, by heating the solution of nitric acid or of a nitrate, for some time with zinc filings, or better with an amalgam of zinc, and then filtering off the liquid: in the dry way, by fusing the substance under examination with carbonate of soda and potassa at a moderate heat, extracting the mass, after cooling, with water, and filtering. On now adding the filtrate to a solution of iodide of potassium mixed with starch-paste, and then adding hydrochloric acid, the liquid becomes blue from the formation of iodide of starch. In making the experiment, the operator has to ascertain whether the solution of iodide of potassium mixes with the hydrochloric acid without being colored blue by it, since this blue coloration would indicate the presence of iodic acid in the iodide of potassium, or of free chlorine in the hydrochloric acid. (Compare § 161, 1.)

§ 163.

b. Chloric Acid (ClO_5).

1. Chloric acid, in its most highly concentrated solution, is a colorless or yellow, oily fluid; its odor resembles that of nitric acid. It first reddens litmus and then bleaches it. Dilute chloric acid is colorless and inodorous.

2. All Chlorates are soluble in water. When chlorates are

heated to redness, the whole of their oxygen escapes and metallic chlorides remain.

3. Heated with *charcoal*, or some organic substance, the chlorates DEFLAGRATE, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with *cyanide of potassium* is heated on platinum foil, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. This experiment should be made with very minute quantities only.

5. Free chloric acid oxidizes and decolorizes *indigo* in the same manner as nitric acid; consequently if the solution of a chlorate is mixed with sulphuric acid and solution of indigo, and the mixture heated, the same reaction is observed as with nitric acid (see § 162, 7).

6. If the solution of a chlorate is colored light-blue with *solution of indigo* in sulphuric acid, a little dilute sulphuric acid added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, thus setting free chlorine or a lower oxide of it, which then decolorizes the indigo.

7. When chlorates are treated with *hydrochloric acid*, the constituents of the two acids transpose, forming water, chlorine, and chlorochloric acid ($2\ Cl\ O_5$, $Cl\ O_3$). Application of heat promotes the reaction. The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas of a very disagreeable odor resembling that of chlorine; the hydrochloric acid acquires a greenish-yellow color. In case the hydrochloric acid had been tinged blue with indigo solution, the color would be at once bleached, even by a very minute quantity of a chlorate.

8. *Concentrated sulphuric acid*, poured over a chlorate, converts two-thirds of the metallic oxide into a sulphate and the remaining one-third into perchlorate; this conversion is attended, moreover, with liberation of chlorochloric acid, which imparts an intensely yellow tint to the sulphuric acid, and betrays its presence also by its odor and the greenish color of the evolved gas [$3\ (K\ O, Cl\ O_5) + 4\ S\ O_3 = (K\ O, 2\ S\ O_3) + K\ O, Cl\ O_7 + (Cl\ O_5, Cl\ O_3)$]. The application of heat must be avoided in this experiment, and the quantities operated upon should be very small, since otherwise the decomposition might take place with such violence as to cause an explosion.

§ 164.

Recapitulation and remarks.—Of the reactions which have been suggested to effect the detection of nitric acid, those with sulphate of protoxide of iron and sulphuric acid, with copper filings and sulphuric acid, with brucia, and also those based upon the reduction of the nitrates to nitrites, give the most positive results; with regard to deflagration with charcoal, detonation with cyanide of potassium, and discoloration of solution of indigo, we have seen that these reactions belong equally to chlorates as to nitrates, and are consequently decisive only when no chloric acid is present. The presence of free nitric acid in a fluid may be detected by evaporating the fluid, in a porcelain dish on the water-bath, to dryness, having first thrown in a few quill-cuttings: yellow coloration of these indicates the presence of nitric acid (*Runge*). The best way to ascertain whether chloric acid is present or not, is to ignite the sample under examination, dissolve the mass, and test the solution with nitrate of silver. If a chlorate is present, this is converted into a chloride upon ignition, and nitrate of silver will now precipitate chloride of silver from the solution. However, the process is thus simple only if no chloride is present along with the chlorate. But in presence of a chloride, the latter must be removed first by adding nitrate of silver to the solution as long as a precipitate continues to form, and filtering the fluid from the precipitate; the filtrate is then, after addition of pure carbonate of soda, evaporated to dryness, and the residue ignited. It is, however, generally unnecessary to pursue this circuitous way, since the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid.

To detect nitric acid in presence of a large quantity of chloric acid, the mixture is mixed with excess of carbonate of soda, evaporated to dryness if necessary, and the residue is ignited with moderate intensity, but long enough to convert all chlorate into chloride. The residual mass is now tested for nitric (or nitrous) acid.

§ 165.

PERCHLORIC ACID ($Cl O_7$).—When anhydrous this acid is a colorless mobile liquid which explodes violently when dropped upon charcoal, and on exposure to the air, forms thick white fumes.—(ROSCOE.) The hydrated acid crystallizes in needles, the concentrated aqueous solution is heavy and has an oily consistence. The dilute solution on distillation yields in the distillate first water, then the dilute, and finally the strong acid. The perchlorates are all soluble in water, most of them with ease; they are all decomposed on ignition, the alkaline perchlorates give off oxygen and alkaline chloride remains. *Potassa salts* produce in not too dilute solutions a white crystalline precipitate of perchlorate of potassa ($KO Cl O_7$), which is difficultly soluble in water and insoluble in alcohol. Salts of *baryta* and *silver* are not affected. Concentrated sulphuric acid does not decompose perchloric acid in the

cold and with difficulty when heated (distinction from chloric acid). Hydrochloric, nitric and sulphurous acids do not decompose an aqueous solution of perchloric acid; previously added indigo solution is, therefore, not decolorized (distinction from all other oxacids of chlorine).

II. Organic Acids.

First Group.

Acids which are invariably precipitated by Chloride of Calcium: *Oxalic Acid*, *Tartaric Acid* (Paratartaric or Racemic Acid), *Citric Acid*, *Malic Acid*.

§ 166.

a. Oxalic Acid.

For the reactions of oxalic acid I refer to § 148.

b. Tartaric Acid ($2\,H\,O, C_8 H_4 O_{10}$).

1. The hydrate of tartaric acid forms colorless crystals of an agreeable acid taste, which are persistent in the air, and soluble in water and in spirit of wine. Tartaric acid when heated to 212° Fah. loses no water, at 340° Fah. it fuses and at a higher temperature becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar. The aqueous solutions of tartaric acid and of nearly all tartrates, produce right-handed rotation of a ray of polarized light.

2. The tartrates with alkaline base are soluble in water, and so are those with the metallic oxides of the third and fourth groups. The solution of tartrate of sesquioxide of iron, when evaporated in the water-bath to the consistence of syrup, deposits a basic salt in the form of powder. The tartrates, which are insoluble in water, dissolve in hydrochloric or nitric acid. The tartrates suffer decomposition when heated to redness; charcoal separates, and the same peculiar odor is emitted as attends the carbonization of free tartaric acid.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *sesquioxide of iron*, *protoxide of manganese* or *alumina* is added in not too large quantity, and then ammonia or potassa, no precipitation of sesquioxide of iron, protoxide of manganese or alumina will ensue, since the double tartrates formed are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other oxides by alkalies.

4. Free tartaric acid produces with *salts of potassa*, and more particularly with the acetate, a difficultly soluble precipitate of bitartrate of potassa. A similar precipitate is formed when acetate of potassa and free acetic acid are added to the solution of a neutral tartrate. The acid tartrate of potassa dissolves

readily in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. The separation of the bitartrate of potassa precipitate is greatly promoted by shaking, or by rubbing the sides of the vessel with a glass-rod. If it is desired to make this reaction delicate, the solution of tartaric acid should be concentrated. If then a few drops are mixed on a watch glass with a drop of strong solution of acetate of potassa and stirred with a glass-rod, the minute crystals of bitartrate of potassa are formed in the track of the rod. Addition of an equal volume of alcohol heightens the delicacy of the reaction.

5. *Chloride of calcium* throws down from solutions of neutral tartrates a white precipitate of TARTRATE OF LIME ($2\ Ca\ O, C_8\ H_4\ O_{10} + 8$ aq.). Presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time (often for a long time). Agitation of the fluid or friction on the sides of the vessel promotes the separation of the precipitate. The precipitate is crystalline or it invariably assumes a crystalline form after some time; it dissolves in a cold not over dilute solution of potassa or soda, pretty free from carbonic acid, to a clear fluid. But upon boiling this solution, the dissolved tartrate of lime separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* produces in solutions of neutral tartrates—and also in a solution of free tartaric acid, if added to alkaline reaction—white precipitates which, flocculent at first, assume afterwards a crystalline form; so long as they remain flocculent, they are readily dissolved by tartaric acid as well as by solutions of chloride of ammonium. From these solutions the tartrate of lime separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of sulphate of lime* fails to produce a precipitate in a solution of tartaric acid; in solutions of neutral tartrates it produces a trifling precipitate after the lapse of some time.

8. If solution of ammonia is poured upon even a very minute quantity of tartrate of lime, a small fragment of crystallized *nitrate of silver* added, and the mixture slowly and gradually heated, the sides of the test-tube are covered with a bright coating of metallic silver. If instead of a crystal, solution of nitrate of silver be used, or heat be applied more rapidly, the reduced silver will separate in pulverulent form (*Arthur Casselmann*).

9. *Acetate of lead* produces white precipitates in solutions of tartaric acid and its salts. The precipitate ($2\ Pb\ O, C_8\ H_4\ O_{10}$) dissolves readily in nitric acid and in ammonia.

10. *Nitrate of silver* does not precipitate free tartaric acid; but in solutions of neutral tartrates it produces a white precipitate of TARTRATE OF SILVER ($2\ Ag\ O, C_8\ H_4\ O_{10}$), which dissolves readily

in nitric acid and in ammonia; upon boiling it turns black, owing to ensuing reduction of the silver to the metallic state.

11. Upon heating hydrated tartaric acid, or a tartrate, with *concentrated sulphuric acid* the sulphuric acid acquires a brown color almost simultaneously with the evolution of gas.

§ 167.

c. Citric Acid (3 H O, $C_{12} H_5 O_{11}$).

1. Crystallized citric acid, obtained by the cooling of its solution, has the formula, 3 H O, $C_{12} H_5 O_{11}$ + 2 aq. It crystallizes in pellucid, colorless, and inodorous crystals of an agreeable acid taste, which dissolve readily in water and in spirit of wine, and effloresce slowly in the air. Heated at 112° F., the crystallized acid loses its water of crystallization; when subjected to the action of a stronger heat, it fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization.

2. The citrates with alkaline base are readily soluble in water, as well in the neutral as in the acid state; solution of citric acid is therefore not precipitated by acetate of potassa. The compounds of citric acid with such of the metallic oxides as are weak bases, sesquioxide of iron, for instance, are also readily soluble in water; solution of citrate of sesquioxide of iron does not deposit basic salt on evaporating in the water bath to a syrupy consistency. Citrates, like tartrates, and for the same reason, prevent the precipitation of sesquioxide of iron, protoxide of manganese, alumina, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of neutral citrate of lime (3 Ca O, $C_{12} H_5 O_{11}$ + 4 aq.) forms immediately upon saturating with potassa or soda the concentrated solution of citric acid, mixed with chloride of calcium in excess. The precipitate is insoluble in potassa, but it dissolves readily in solution of chloride of ammonium; upon boiling this chloride of ammonium solution, neutral citrate of lime of the same composition separates again in the form of a white crystalline precipitate, which, however, is now no longer soluble in chloride of ammonium. If a solution of citric acid mixed with chloride of calcium is saturated with ammonia, a precipitate will form in the cold only after many hours' standing; but upon boiling the clear fluid, neutral citrate of lime of the properties just stated will suddenly precipitate. When citrate of lime is heated with ammonia and nitrate of silver, no reduction of the latter salt ensues.

4. *Lime-water* produces no precipitate in cold solutions of citric

acid or of citrates. But upon heating the solution to boiling, with a tolerable excess of hot prepared lime-water, a white precipitate of CITRATE OF LIME is formed, of which the greater portion redissolves upon cooling.

5. *Acetate of lead*, when added in excess to a solution of citric acid, produces a white precipitate of CITRATE OF LEAD (3 Pb O, $C_{12} H_5 O_{11}$), which, after washing, dissolves readily in ammonia.

6. *Nitrate of silver* produces in solutions of neutral citrates of the alkalies a white, flocculent precipitate of CITRATE OF SILVER (3 Ag O, $C_{12} H_5 O_{11}$), which does not become black on boiling.

7. Upon heating citric acid or citrates with *concentrated sulphuric acid*, carbonic oxide and carbonic acid escape at first, the sulphuric acid retaining its natural color; upon continued ebullition, however, the solution acquires a dark color, and sulphurous acid is evolved.

§ 168.

d. MALIC ACID (2 H O, $C_4 H_4 O_5$).

1. HYDRATE OF MALIC acid crystallizes with great difficulty, forming crystalline crusts, which deliquesce in the air, and dissolve readily in water and in alcohol. Exposed to a temperature of 300° Fah., hydrated malic acid loses 2 eq. of water, and slowly passes into hydrated FUMARIC ACID (2 H O, $C_4 H_2 O_4$); by heating to 356° Fah. it is resolved into water, MALEIC ACID (2 H O, $C_8 H_2 O_6$) which volatilizes, and fumaric acid which remains behind; if, finally, the temperature exceeds 392° Fah., the fumaric acid also volatilizes. This deportment of malic acid is highly characteristic. If the experiment is made in a small spoon, pungent acid vapors are evolved with frothing effervescence. If the experiment is made in a small tube, maleic acid first, and afterward fumaric acid will condense to crystals in the colder part of the tube.

2. Malic acid forms with most bases SALTS soluble in water. The acid malate of potassa is not very difficultly soluble in water, hence solution of malic acid is not precipitated by acetate of potassa. Malic acid prevents, like tartaric acid, the precipitation of sesquioxide of iron, &c., by alkalies.

3. *Chloride of calcium* fails to produce a precipitate in solutions of free malic acid. Even after saturation with potassa or soda no precipitate is formed. But upon boiling, a precipitate of MALATE OF LIME (2 Ca O, $C_8 H_4 O_8$ + 6 aq.) separates from concentrated solutions. If the precipitate is dissolved in a very little hydrochloric acid, ammonia added to the solution, and the fluid boiled, the malate of lime separates again; but if it is dissolved in a somewhat larger quantity of hydrochloric acid, it will not reprecipitate, after addition of ammonia in excess, even upon continued

boiling. Alcohol precipitates it immediately from a solution of the kind. Malate of lime, when heated with ammonia and nitrate of silver, nearly or altogether fails to effect the reduction of the latter to the metallic state.

4. *Lime-water* produces no precipitate, either in solutions of free malic acid or in solutions of malates. Even on boiling, the liquid remains clear, if the lime-water was prepared with boiling water.

5. *Acetate of lead* throws down from solutions of malic acid and of malates a white precipitate of MALATE OF LEAD ($2\ Pb\ O, C_3\ H_4\ O_5 + 6$ aq.). The precipitation is the most complete, if the fluid is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the fluid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, the remainder fuses to a mass resembling resin melted under water. This reaction is distinctly marked only when the malate of lead is tolerably pure; if mixed with other salts of lead—if, for instance, ammonia is added to alkaline reaction, it is only imperfect or fails altogether to make its appearance.

6. *Nitrate of silver* throws down from solutions of neutral malates of the alkalies a white precipitate of MALATE OF SILVER, which upon boiling turns a little gray.

7. Upon heating malic acid with *concentrated sulphuric acid*, carbonic acid and carbonic oxide gas are evolved at first; the fluid then turns brown and ultimately black, with evolution of sulphurous acid.

§ 169.

Recapitulation and remarks.—Of the organic acids of this group, *oxalic acid* is characterized by the precipitation of its lime-salt from its solution in hydrochloric acid by ammonia, and also by acetate of soda, as well as by the immediate precipitation of the free acid by solution of sulphate of lime. *Tartaric acid* is characterized by the difficult solubility of the acid potassa salt, the solubility of the lime salt in cold solution of soda and of potassa, the deportment of the lime salt with ammonia and nitrate of silver, and the peculiar odor which the acid and its salts emit upon heating. In presence of the other acids it is most certainly detected by aid of acetate of potassa (§ 166, 4). *Citric acid* is most strongly characterized by its deportment with lime-water, or with chloride of calcium and ammonia in presence of chloride of ammonium. But for its detection, oxalic and tartaric acids must have been previously removed from the solution. *Malic acid* would be sufficiently characterized by the deportment of malate of lead when heated under water, were this reaction more sensitive, and not so easily prevented by

the presence of other acids. The safest means of identifying malic acid is to convert it into malæic acid by heating in a glass tube; but this conversion can be effected successfully only with pure hydrate of malic acid. Malate of lead is difficultly soluble in ammonia, whilst citrate and tartrate of lead dissolve readily in that agent; this different deportment of the lead salts of the acids affords also a means of distinguishing malic from citric and tartaric acids. If only one of the four acids is present in a solution, lime-water will suffice to indicate which of the four is present; since malic acid is not precipitated by this reagent, citric acid only upon boiling, tartaric acid and oxalic acid already in the cold; and the tartrate of lime redissolves upon addition of chloride of ammonium, whilst the oxalate does not. If the four acids together are present in a solution, the oxalic acid and tartaric acid are precipitated first by chloride of calcium and ammonia, in presence of chloride of ammonium (the tartrate of lime separates under these circumstances completely only after some time; it is separated from the oxalate by treating with solution of soda); the citrate of lime is then thrown down by boiling, and the malate finally by means of spirit of wine. (The precipitate produced by spirit of wine must never be taken positively for malate of lime, without further proof, since the sulphate and other salts of lime are also precipitated by that agent under the same circumstances. Positive conviction can only be attained by the production of hydrate of malic acid from the lime-salt. To effect this, the precipitate is dissolved in acetic acid, spirit of wine added, and the fluid filtered, if necessary. The filtrate is precipitated with acetate of lead, the fluid neutralized with ammonia, the precipitate washed, stirred in water, decomposed by hydrosulphuric acid, and the filtrate evaporated to dryness.)

To find a little citric or malic acid in presence of much tartaric acid, the latter is first thrown down by acetate of potassa with addition of an equal volume of strong alcohol. From the filtrate, the other acids may be precipitated by chloride of calcium if some more alcohol be added.

§ 170.

Racemic Acid, or Paratartaric Acid ($2\,H\,O, C_8 H_4 O_{10}$).

The formula of crystallized racemic acid is $2\,H\,O, C_8 H_4 O_{10} + 2$ aq. The crystallization water escapes slowly in the air, but rapidly at 212° F. (difference between racemic acid and tartaric acid). Towards solvents racemic acid comports itself like tartaric acid. The racemates also show very similar deportment to that of the tartrates. However, many of them differ in the amount of water they contain, and in form and solubility from the corresponding tartrates. Aqueous solutions of racemic acid and racemates do not deviate the ray of polarized light. *Chloride of calcium* precipitates from the solutions of free racemic acid, and of racemates racemate of lime ($2\,Ca\,O, C_8 H_4 O_{10} + 8$ aq.), as a white crystalline powder. Ammonia throws

down the precipitate from its solution in hydrochloric acid, either immediately or at least very speedily (difference between racemic acid and tartaric acid). It dissolves in solution of soda and potassa, but is reprecipitated from this solution by boiling (difference between racemic acid and oxalic acid). *Lime-water* added in excess, produces immediately a white precipitate insoluble in chloride of ammonium (difference between racemic acid and tartaric acid). *Solution of sulphate of lime* does not immediately produce a precipitate in a solution of racemic acid (difference between racemic acid and oxalic acid); however, after ten or fifteen minutes, racemate of lime separates (difference between racemic acid and tartaric acid); in solutions of neutral racemates the precipitate forms immediately. With *salts of potassa* racemic acid comports itself like tartaric acid.

If a solution of the double racemate of soda and potassa, or of the racemate of soda and of ammonia, is allowed to crystallize slowly, two kinds of crystals are obtained which differ from each other in appearance as the direct image of an object differs from its image reflected from a mirror. One set of (dextro-hemihedral) crystals contains the ordinary (right polarizing) tartaric acid (dextro-tartaric acid), the other (lævo-hemihedral) crystals contain an acid which scarcely differs from ordinary tartaric acid except that it rotates the plane of polarization to the left. It is termed lævo-tartaric acid. When the two kinds of crystals are dissolved together, the solution has all the reactions of racemic acid.

SECOND GROUP OF THE ORGANIC ACIDS.

Acids which Chloride of Calcium fails to precipitate under any Circumstances, but which are precipitated from Neutral Solutions by Sesquichloride of Iron; *Succinic Acid*, *Benzoic Acid*.

§ 171.

a. Succinic Acid ($2\,H\,O, C_8 H_4 O_6$).

1. Hydrate of Succinic acid forms colorless and inodorous prisms or tables of slightly acid taste, which are readily soluble in water, alcohol, and ether, difficultly soluble in nitric acid, and volatilize when exposed to the action of heat, leaving only a little charcoal behind. The officinal acid has an empyreumatic odor, and leaves a somewhat larger carbonaceous residue upon volatilization. Succinic acid is not destroyed by heating with nitric acid, and may therefore be easily obtained in the pure state by boiling with that acid for half an hour, by which means the oil of amber, if present, will be destroyed. By sublimation crystalline needles of silky lustre are obtained; the hydrate loses water in this process, so that by repeated sublimation anhydrous acid is ultimately obtained. Heated in the air, succinic acid burns with a blue flame, free from soot.

2. The succinates are decomposed at a red heat; those which have an alkali or alkaline earth for base, are converted into carbonates in this process, the change being attended with separation of charcoal. Most of the succinates are soluble in water.

3. *Sesquichloride of iron* produces in solutions of neutral succi-

nates of the alkalies a brownish pale-red, bulky precipitate of SUCCINATE OF SESQUIOXIDE OF IRON ($Fe_2 O_3$, $C_8 H_4 O_6$); one-third of the succinic acid is liberated in this reaction, and retains part of the precipitate in solution, if the fluid is filtered off hot. The precipitate dissolves readily in mineral acids; ammonia decomposes it, causing the separation of a less bulky precipitate of a highly basic succinate of sesquioxide of iron, and combining with the greater portion of the acid to succinate of ammonia, which dissolves.

4. *Acetate of lead* gives with succinic acid a white precipitate of neutral SUCCINATE OF LEAD (2 Pb O, $C_8 H_4 O_6$), which is very sparingly soluble in water, acetic acid, and succinic acid, but dissolves readily in solution of acetate of lead and in nitric acid. Treated with ammonia, the neutral succinate of lead is converted into a basic salt (6 Pb O, $C_8 H_4 O_6$).

5. A mixture of *alcohol*, *ammonia*, and *solution of chloride of barium* produces in solutions of free succinic acid and of succinates a white precipitate of SUCCINATE OF BARYTA (2 Ba O, C $H_4 O_6$).

6. *Nitrate of suboxide of mercury* and *nitrate of silver* also precipitate the succinates; the precipitates, however, are not possessed of any characteristic properties.

§ 172.

b. BENZOIC ACID (H O, $C_{14} H_6 O_3$).

1. Pure HYDRATE OF BENZOIC ACID forms inodorous white scales or needles, or simply a crystalline powder. When heated, it fuses, and afterwards volatilizes completely. The fumes of benzoic acid cause a peculiar irritating sensation in the throat, and provoke coughing; when cautiously cooled, they condense to brilliant needles, when kindled, they burn with a luminous sooty flame. The common officinal hydrate of benzoic acid has the odor of benzoin, and leaves a small carbonaceous residue upon volatilization. Hydrate of benzoic acid is very sparingly soluble in cold water, but it dissolves pretty readily in hot water and in alcohol. Addition of water, therefore, imparts a milky turbidity to a saturated solution of benzoic acid in alcohol.

2. Most of the BENZOATES are soluble in water; only those with weak bases, *e. g.*, sesquioxide of iron, are insoluble. The soluble benzoates have a peculiar, pungent taste. The addition of a *strong acid* to aqueous solutions of benzoates dispels the benzoic acid, which separates as hydrate in the form of a dazzling white, sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates, by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. *Sesquichloride of iron* precipitates solutions of free benzoic acid incompletely; solutions of neutral benzoates of the alkalies completely. The precipitate of BENZOATE OF SESQUIOXIDE OF

IRON ($2\ Fe_2\ O_3$, $3\ [C_{14}\ H_3\ O_3] + 15$ aq.) is bulky, flesh-colored, insoluble in water. It is decomposed by ammonia in the same manner as succinate of sesquioxide of iron, from which salt it differs in this, that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid.

4. *Acetate of lead* fails to precipitate free benzoic acid and benzoate of ammonia, at least immediately; but it produces white, flocculent precipitates in solutions of benzoates with a fixed alkaline base.

5. A mixture of *alcohol*, *ammonia*, and *solution of chloride of barium* produces NO precipitate in solutions of free benzoic acid or of the alkaline benzoates.

§ 173.

Recapitulation and remarks.—Succinic and benzoic acids are distinguished from all other acids by the facility with which they may be sublimed, and by their deportment with sesquichloride of iron. They are distinguished from one another by the different color of their salts with sesquioxide of iron, and also by their different deportment with chloride of barium and alcohol; but principally by their different degrees of solubility, succinic acid being readily soluble in water, whilst benzoic acid is very difficult of solution. Succinic acid is seldom perfectly pure, and may therefore often be detected by the odor of oil of amber which it emits.

The detection of the two acids, when present in the same solution with other acids, may be effected as follows: precipitate with sesquichloride of iron, warm the washed precipitate with ammonia, filter, concentrate the solution, divide it into two parts, and mix one part with hydrochloric acid, the other with chloride of barium and alcohol.

Succinic acid and benzoic acid do not prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

THIRD GROUP OF THE INORGANIC GROUP.

ACIDS WHICH ARE NOT PRECIPITATED BY CHLORIDE OF CALCIUM NOR BY SESQUICHLORIDE OF IRON: *Acetic Acid*, *Formic Acid*. (Lactic Acid, Propionic Acid, Butyric Acid).

§ 174.

a. ACETIC ACID ($H\ O,\ C_4\ H_3\ O_3$).

1. The HYDRATE OF ACETIC ACID forms transparent crystalline scales, which fuse at 62·6° F. to a colorless fluid of a peculiar, pungent and penetrating odor, and exceedingly acid taste. When exposed to the action of heat, it volatilizes completely, forming pungent inflammable vapors, which burn with a blue flame. It is

miscible with water in all proportions; it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The ACETATES undergo decomposition at a red heat; among the products of this decomposition we generally find hydrate of acetic acid, and almost invariably acetone ($C_6 H_6 O_2$). The acetates of the alkalies and alkaline earths are converted into carbonates in this process; of the acetates with metallic bases many leave the metal behind in the pure state, others in the form of oxide. Most of the residues which the acetates leave upon ignition are carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are difficult of solution in that menstruum. If acetates are distilled with dilute sulphuric acid, the free acetic acid is obtained in the distillate.

3. If *sesquichloride of iron* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with sesquichloride of iron, the fluid acquires a deep dark-red color, owing to the formation of ACETATE OF SESQUIOXIDE OF IRON. Upon boiling, the fluid becomes colorless if it contains an excess of acetate, the whole of the sesquioxide of iron precipitating as a basic acetate, in the form of brown-yellow flocks. Ammonia precipitates from it the whole of the sesquioxide of iron as hydrate. Upon addition of hydrochloric acid, a fluid which appears red from the presence of acetate of sesquioxide of iron turns yellow (difference from sulphocyanide of iron).

4. Neutral acetates (but not free acetic acid) give with *nitrate of silver* white, crystalline precipitates of ACETATE OF SILVER (Ag O, $C_4 H_3 O_3$), which are very sparingly soluble in cold water. They dissolve more easily in hot water, but separate again upon cooling, in the form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

5. *Nitrate of suboxide of mercury* produces in solutions of acetic acid, and more readily still in solutions of acetates, white, scaly crystalline precipitates of ACETATE OF SUBOXIDE OF MERCURY (Hg_2 O, $C_4 H_3 O_3$), which are sparingly soluble in water and acetic acid, in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water upon heating, but separate again upon cooling, in the form of small crystals; in this process the salt undergoes partial decomposition: a portion of the mercury separates in the metallic state, and imparts a gray color to the precipitate. If the acetate of suboxide of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. *Chloride of mercury* heated with solutions of acetic acid or of acetates yields no precipitate of subchloride of mercury.

7. When acetates are heated with *concentrated sulphuric acid*,

HYDRATE OF ACETIC ACID is evolved, which may be known by its pungent odor. But if the acetates are heated with a mixture of about equal volumes of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER ($C_4 H_5 O, C_4 H_3 O_3$) is formed. The odor of this ether is highly characteristic and agreeable; it is most distinct upon shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odor of the free acetic acid.

7. If acetates are distilled with dilute sulphuric acid, and the distillate is digested with an excess of oxide of lead, part of the latter dissolves as basic acetate of lead, which may be readily recognised by its alkaline reaction.

§ 175.

b. FORMIC ACID ($H O, C_2 H O_3$).

1. The HYDRATE OF FORMIC ACID is a transparent, colorless, slightly fuming liquid, of a characteristic and exceedingly penetrating odor. When cooled to below 32° F., it crystallizes in colorless plates. It is miscible in all proportions with water and with alcohol. When exposed to the action of heat, it volatilizes completely; the vapors are inflammable and burn with a blue flame.

2. The FORMATES, like the corresponding acetates, leave upon ignition either carbonates, oxides, or metals behind, the process being attended with separation of charcoal, and escape of carbide of hydrogen, carbonic acid, and water. All the compounds of formic acid with bases are soluble in water; alcohol likewise dissolves some of them.

3. Formic acid presents the same deportment with *sesquichloride of iron* as acetic acid.

4. *Nitrate of silver* fails to precipitate free formic acid, and affects the alkaline formates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of FORMATE OF SILVER ($Ag O, C_2 H O_3$) acquires very rapidly a darker tint, owing to the separation of metallic silver. Complete reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time; but immediately, upon applying heat to the fluid containing the precipitated formate of silver. The same reduction of the oxide of silver to the metallic state takes place in a solution of free formic acid, and also in solutions of formates so dilute that the addition of the nitrate of silver failed to produce a precipitate in them. But it does not take place in presence of an excess of ammonia. The rationale of this reduction is as follows: the formic acid, which may be looked upon as a compound of carbonic oxide with water, deprives the oxide of silver of its oxygen, thus causing the formation of carbonic acid, which

escapes, and of water, whilst the reduced silver separates in the metallic state.

5. *Nitrate of suboxide of mercury* gives no precipitate with free formic acid; but in concentrated solutions of alkaline formates this reagent produces a white, sparingly soluble precipitate of FORMATE OF SUBOXIDE OF MERCURY (Hg_2O, C_2 H O_3), which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction is also attended with the formation of carbonic acid and water, and takes place, the same as with the oxide of silver, both in solutions of free formic acid and in fluids so highly dilute that the formate of suboxide of mercury is retained in solution.

6. If formic acid or an alkaline formate is heated with *chloride of mercury* to from 140° to 158° F., SUBCHLORIDE OF MERCURY precipitates. Free hydrochloric acid, as well as a large quantity of alkaline chlorides prevent this reaction.

7. If formic acid or a formate is heated with *concentrated sulphuric acid*, the formic acid is resolved into water and carbonic oxide gas, which latter escapes with effervescence, and if kindled, burns with a blue flame. The fluid does not turn black in this process. The rationale of the decomposition of the formic acid is this: the sulphuric acid withdraws from the formic acid the water or the oxide necessary for the existence of the latter acid, and thus occasions a transposition of its elements (C_2 H O_3 = 2 C O + H O). Upon heating formates with dilute sulphuric acid in a distilling apparatus, free formic acid is obtained in the distillate, and may mostly be readily detected by its odor. Upon heating a formate with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack-like smell.

8. If dilute formic acid is heated with *oxide of lead*, the latter dissolves. On cooling the solution, which, if necessary, is concentrated by evaporation, the FORMATE OF LEAD (Pb O, C_2 H O_3) separates in brilliant prisms or needles.

§ 176.

Recapitulation and remarks.—Acetic acid and formic acid may be distilled over with water, and form with sesquioxide of iron soluble neutral salts which dissolve in water, imparting to the fluid a blood-red color, and are decomposed upon boiling. These reactions distinguish the two acids of the third group from the other organic acids. From each other the two acids are distinguished by the odor of their hydrates and ethyle compounds, and by their different deportment with salts of silver and salts of mercury, oxide of lead, and concentrated sulphuric acid. The separation

of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of oxide of mercury or oxide of silver. Formic acid reduces the oxides, and suffers decomposition, being resolved into carbonic oxide and water; whilst the acetic acid combines with the oxides, forming acetates, which remain in solution.

§ 177.

More rarely occurring Organic Acids of the Third Group.

1. LACTIC ACID (2 H O, C_{12} H_{10} O_{10}) is found in some of the liquids of the animal body, in milk and in vegetable juices which have soured. When pure, its hydrate is a syrupy liquid which has no odor, but possesses a purely acid and biting taste. When slowly heated, at 266° Fah., it yields a distillate of water and a little hydrated acid, and leaves a residue of lactic anhydride (C_{12} H_{10} O_{10}), which at higher temperatures (480°–570° Fah, is resolved into carbonic oxide, carbonic acid, lactide and other products. Lactic acid dissolves with ease in water, alcohol and ether. On boiling the aqueous solution a portion of the acid escapes with the vapors of water. The lactates are all soluble in water and alcohol, most of them, however, with difficulty. In ether they are all insoluble. The best mode of proceeding for the detection of lactic acid consists in preparing certain of its salts, and observing their form under the microscope. The salts best adapted for this purpose are those of lime and zinc. To prepare the lime salt from animal or vegetable juices the method of *Scherer* is to be recommended. The liquid is diluted if needful with water, treated with baryta water, and filtered from the precipitate. The filtrate is distilled with a little sulphuric acid (to remove volatile acids) and the residue is digested for several days with strong alcohol. The acid solution is distilled with addition of milk of lime, filtered warm from the excess of lime and from precipitated sulphate of lime, and subjected to a stream of carbonic acid gas, again heated to boiling, and filtered from carbonate of lime, and evaporated to dryness. The residue is warmed and digested with strong alcohol, filtered, and the neutral filtrate set aside for some days for the lactate of lime to deposit. If so little lactic acid be present that no crystals separate, the liquid is evaporated to the consistence of syrup, strong alcohol is added, the mixture allowed to stand some time, and the alcoholic solution poured or filtered into a stoppered vessel, and a small quantity of ether is added by degrees. By this treatment even traces of lactate of lime may be brought to crystallization. Under the microscope this salt appears in tufts of needles, of which there are always some specimens that resemble two brushes joined base to base. Lactate of zinc when rapidly deposited appears under the microscope in the form of globular groups of needles. When it crystallizes slowly it at first yields crystals with curved faces, and narrower at one end than at the other, like a club. Their crystals gradually increase in size, the extremities become narrower, while the middle thickens (*Fienke*).

2. PROPIONIC ACID (H O, C_6 H_5 O_3) and 3 BUTYRIC ACID (H O, C_8 H_7 O_3). Propionic acid is produced under a great variety of circumstances, it is found especially in fermented liquids. The pure hydrated acid crystallizes in minute plates, [redacted] at 284–288° Fah., is easily soluble in water, upon hydrated phosphoric acid [redacted]loride of calcium solution, it floats as an oily layer. It has a peculiar odor, reminding at once of acetic and butyric acids. On distilling its aqueous solution, it passes over with the water. Butyric acid occurs in animal and vegetable matters, especially in fermented liquids of the most various kinds. The pure hydrate is a colorless, mobile, caustic, very sour liquid which boils at about 320° Fah., and has a disagreeable odor, partaking of that of rancid butter and acetic acid. It is soluble in water and alcohol in all proportions; from concentrated aqueous

solutions it is separated by chloride of calcium, strong acids, &c., in the form of a thin oil. Its odor is especially marked in its aqueous solution. It distils over when heated with water.

Propionic and butyric acids occur in fermented liquids, in guano and in many mineral waters, often associated with formic and acetic acids. In such mixtures one may operate as follows, to detect the individual acids: The substance, sufficiently diluted with water, is acidulated with sulphuric acid and distilled. The distillate is saturated with baryta water, evaporated to dryness, and the residue repeatedly extracted with boiling alcohol of 85 *per cent.* By this means a solution is obtained in which exist the propionate, butyrate, and a part of the acetate of baryta, while the formate and a part of the acetate remain undissolved. The alcoholic solution is evaporated to dryness, the residue dissolved in water, decomposed by cautious addition of sulphate of silver (of which not quite enough to throw down the baryta, rather than an excess, should be employed), boiled, filtered, and the solution evaporated in a desiccator. The crystals which form at first, an intermediate crop, and a final crop, are collected and examined separately. The acetate of silver when dissolved in concentrated sulphuric acid, gives the odor of acetic acid, and no oily droplets; propionate and butyrate of silver under the same treatment yield oil-drops (in small quantities to be recognized only by the help of a microscope), and further, give the odor peculiar to these acids. In order, however, to decide with certainty between propionic and butyric acids, it is necessary to determine the per centage of silver in the salts separated by crystallization, and thence calculate the atomic weight of the acids.

In a solution which contains a large quantity of acetic acid with but little propionic and butyric acids, that portion of the baryta salts taken up by alcohol is brought into aqueous solution, from it the baryta is exactly thrown down by sulphuric acid; one-half of the acid solution is now neutralized by carbonate of soda, the other half added and the whole subjected to distillation. The distillate which contains, principally, the propionic and butyric acids is saturated with baryta, decomposed by sulphate of silver and further treated as above directed.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PART II.

PRELIMINARY REMARKS

ON THE

COURSE OF QUALITATIVE ANALYSIS IN GENERAL AND ON THE PLAN OF THIS PART OF THE PRESENT WORK IN PARTICULAR.

The knowledge of reagents and of the deportment of other bodies with them enables us to ascertain at once whether a compound of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. Thus, for instance, a few simple reactions suffice to show whether a body which appears to be calcareous spar, is really carbonate of lime, and that another, which we hold to be gypsum, *is* actually sulphate of lime. This knowledge usually suffices also to ascertain whether a certain body is present or not in a compound; for instance, whether or not a white powder contains subchloride of mercury. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all* the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected in a mixture or compound, no other substance *can* possibly be present—if consequently a *complete qualitative analysis* is our object, the mere knowledge of the reagents, and of the reactions of other bodies with them, will not suffice for the attainment of this end; this requires the additional knowledge of a systematic and progressive course of analysis, in other words, the knowledge of the *order* and *succession* in which solvents, and general and special reagents, should be applied, both to effect the speedy and certain detection of every component element of a compound or mixture, and to prove with certainty the absence of all other substances. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method whatever in our investigations and experiments, analyzing becomes (at least in the hands of a novice) mere guess-work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method. But it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. However, all analytical methods agree in this, that the substances present or supposed to be present in a compound or mixture, are in the first place classed into certain groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order and succession in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a certain definite course, or system, of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will in certain given cases most readily and rapidly lead to the attainment of the object in view.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the *First Section* of the second part of this work.

The elements and compounds comprised in it are the same which we have studied in Part I., with the exception of those given in that part simply by way of appendix, or printed in smaller type.

The *First Section* of the Second Part consists of PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein I have laid down a systematic course which, with due care and attention, will, by progressive steps, lead speedily and safely to the attainment of the end in view.

The subdivisions of this practical course are:

1, Preliminary examination;

2, Solution;

3, Actual analysis.

The third subdivision (the *actual analysis*) is again subdivided into, (1) Examination of compounds in which but one base and one acid are assumed to be present; and, (2) Examination of mixtures or compounds in which all the substances treated of in the present work are assumed to be present. With respect to the latter section, I have to remark that where the preliminary examination has not clearly demonstrated the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made in consequence of the reactions

observed. In cases where the intention is simply to test a compound or mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular numbers which ought to be attended to.

As the construction of a universally applicable systematic course of analysis requires due regard to, and provision for, every contingency that may possibly arise, it is self-evident that, though in the system here laid down the various bodies comprised in it have been assumed to be mixed up together in every conceivable way, it was absolutely indispensable to proceed throughout upon the supposition that no foreign *organic* matters whatever were present, since the presence of such matters would of course tend to prevent or obscure many reactions, and variously modify others.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, with a very few exceptions, still there are special cases in which it may be advisable to modify it. A preliminary treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with; the presence of coloring, slimy, organic matters more especially requires certain preliminary operations.

Not to leave the student without a guide in these special cases, the *Second Section* of this Part will be found to contain a detailed description of the methods employed to effect the analysis of a few important compounds and mixtures which chemists are frequently called upon to examine. Some of these methods show how the analytical process becomes simplified as the number of substances decreases to which regard must be had in the analysis.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depend, since this knowledge alone can furnish the student with a guide to the selection of the proper reagents, and the order in which they ought to be applied, I have given in the *Third Section* of the Second Part an explanation and elucidation of the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, I strongly recommend students to make themselves early and thoroughly acquainted with it. I have devoted a special section to this theoretical explanation of the process, as I think it will be understood better in a connected form, than it would have been by explanatory additions to the several paragraphs, which, moreover might have materially interfered with the plainness and perspicuity of the plan of the practical process.

In this *Third Section* I have also indicated in what residues, solutions, precipitates, &c., as obtained in the systematic course, the operator may look for the elements of more rare occurrence,

and how these bodies may be systematically and surely detected in analyses where they are likely to be present.

SECTION I.

PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. Preliminary Examination.*

§ 178.

1. Examine, in the first place, the physical properties— 1†
color, shape, hardness, gravity, odor, &c.—of the substance intended for analysis, since these will often enable you in some measure to infer its nature. Before proceeding to the application of any chemical process, you must always consider how much of the substance to be analyzed you have at command, since it is necessary, at this early period of the examination, to calculate the quantity which may safely be used in the preliminary investigation. A reasonable economy is in all cases advisable, even though you may possess the substance in large quantities; but, under all circumstances, let it be a fixed rule, never to use at once the whole of what you possess of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments.

A. The Body under Examination is Solid.

I. It is neither a Pure Metal nor an Alloy.

§ 179.

1. The substance is fit for examination if in powder or in 2
minute crystals; but if in larger crystals or in solid pieces, it is necessary in the first place to reduce a portion of it *to fine powder*, if practicable. Bodies of the softer kind may be triturated in a porcelain mortar; those of a harder nature must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then be triturated in an agate mortar.

2. Put some of the powder into a glass tube, sealed 3
at one end, about 2 inches long and $\frac{3}{16}$ths of an inch wide, and heat, first gently over the spirit or gas-lamp, then intensely in the blowpipe flame. The reactions resulting may

* Consult also the observations and additions in the Third Section.

† These marginal numbers are simply intended to facilitate reference.

lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; it often occurs that several of them are observed in the case of one and the same substance.

a. THE SUBSTANCE REMAINS UNALTERED: absence of 4
organic matters, salts containing water of crystallization, readily fusible matters, and volatile bodies.

b. THE SUBSTANCE DOES NOT FUSE AT A MODERATE 5
HEAT, BUT SIMPLY CHANGES COLOR. From white to yellow, turning white again on cooling, indicates OXIDE OF ZINC: from white to yellowish-brown, turning to a dirty light yellow on cooling, indicates BINOXIDE OF TIN; if the color changes from white or reddish-yellow to brownish-red, turning to yellow on cooling, and the body is fusible at a red heat, this indicates the presence of OXIDE OF LEAD; if the color changes from white to orange-yellow, or a deeper and more reddish tint, up to reddish-brown, turning pale yellow on cooling, and the body fuses at an intense red heat, this indicates the presence of TEROXIDE OF BISMUTH; if the color changes from red to black, turning red again on cooling, this indicates the presence of SESQUIOXIDE OF IRON; if from yellow to dark orange the substance being fusible at a strong heat, it indicates NEUTRAL CHROMATE OF POTASSA, &c.

c. THE SUBSTANCE FUSES WITHOUT EXPULSION OF AQUE- 6
OUS VAPOR. If on intense heating, gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, NITRATES OR CHLORATES may be assumed to be present.

d. AQUEOUS VAPORS ARE EXPELLED, WHICH CONDENSE 7
IN THE COLDER PART OF THE TUBE: this indicates the presence either (α) of SUBSTANCES CONTAINING WATER OF CRYSTALLIZATION, in which case they will generally readily fuse, and re-solidify after expulsion of the water; many of these swell considerably whilst yielding up their water, *e. g.* (borax, alum); or (β) of decomposable HYDRATES, in which case the bodies often will not fuse; or (γ) of anhydrous salts, holding water, *mechanically enclosed* between their lamellæ—in which case the bodies will decrepitate; or (δ) of bodies with moisture externally adhering to them.

Test the reaction of the condensed fluid in the tube: if it is alkaline, ammonia may be assumed to be present; if acid, a volatile acid (sulphuric acid, sulphurous acid, hydrofluoric acid, hydrochloric, hydrobromic, or hydriodic acids, nitric acid, &c.).

e. GASES OR FUMES ESCAPE. Observe whether they have a color, smell, acid or alkaline reaction, whether they are inflammable, &c. 8

aa. OXYGEN. The disengagement of this gas indicates the presence of peroxides, chlorates, nitrates, &c. A glimmering slip of wood is relighted in the gaseous current.

bb. SULPHUROUS ACID. This is often produced by the decomposition of sulphates; it may be known by its peculiar odor and by its acid reaction.

cc. HYPONITRIC ACID, resulting from the decomposition of nitrates, especially with oxides of the heavy metals; it may be known by the brownish-red color of the fumes.

dd. CARBONIC ACID. The evolution of carbonic acid indicates the presence of carbonates decomposable by heat [or if accompanied by carbonization (see 10) of organic bodies]. The gas evolved is colorless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

ee. CARBONIC OXIDE GAS. The escape of this gas indicates the presence of oxalates, and, when attended with actual carbonization, also of formates. The gas burns with a blue flame. When evolved from oxalates, it is mingled with carbonic acid, and is more difficult to kindle. Oxalates when placed with a little water and pulverized binoxide of manganese on a watch-glass and a few drops of oil of vitriol added, effervesce from evolution of carbonic acid, formates do not.

ff. CYANOGEN. The evolution of cyanogen gas denotes the presence of cyanides decomposable by heat. The gas may be known by its odor, and the crimson flame with which it burns.

gg. HYDROSULPHURIC ACID GAS. The escape of hydrosulphuric acid gas indicates the presence of sulphides containing water; the gas may be readily known by its odor.

hh. AMMONIA, resulting from the decomposition of ammoniacal salts, or also of cyanides or nitrogenous organic matters, in which latter cases browning or carbonization of the substance takes place, and either cyanogen or offensive empyreumatic oils escape with the ammonia.

f. A SUBLIMATE FORMS. This indicates the presence of volatile bodies: the following are those more frequently met with:— 9

aa. SULPHUR. Separated from mixtures or from many of the metallic sulphides. Sublimes in reddish-brown drops which become solid on cooling, and turn yellow, or yellowish-brown.

bb. AMMONIA SALTS give white sublimates; heated with soda and a drop of water on platinum foil, they evolve ammonia.

cc. MERCURY and compounds of mercury. METALLIC MERCURY forms globules; SULPHIDE OF MERCURY is black, but acquires a red tint when rubbed; CHLORIDE OF MERCURY fuses before volatilizing; SUBCHLORIDE OF MERCURY sublimes without previous fusion; the sublimate, which is yellow whilst hot, turns white on cooling. The red IODIDE OF MERCURY gives a yellow sublimate.

dd. ARSENIC and compounds of that metal. METALLIC ARSENIC forms the well-known arsenical mirror; ARSENIOUS ACID forms small shining crystals; the SULPHIDES OF ARSENIC give sublimates which are reddish-yellow whilst hot, and turn yellow on cooling.

ee. TEROXIDE OF ANTIMONY fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

ff. BENZOIC ACID and SUCCINIC ACID, which may be known by the odor of their fumes.

gg. HYDRATED OXALIC ACID. White crystalline sublimate, thick fumes in the tube. Heating a small sample on platinum foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

g. CARBONIZATION TAKES PLACE: organic substances. 10
This is always attended with evolution of gases (in the case of acetates, of acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkalies or alkaline earths. [Since the observations suggested by this paragraph will decide the operator, whether or not to look for an organic acid in the subsequent analysis, it may be well to caution the beginner not to be too hasty in concluding that carbonization does or does not occur. In addition to what is stated above, we may mention that: 1. *Blackening* is not necessarily carbonization, for salts of volatile acids with certain oxides, as those of copper, nickel and cobalt, blacken on ignition from separation of the oxide. 2.

Carbonization, *i. e.*, the separation of carbon, is usually attended with the disengagement of vapors, which often condense in oily droplets, or as an oily film on the cold part of the tube, and which have a "burnt" odor. 3. The carbon remaining after these vapors cease to escape usually takes fire when heated in contact with the air, and *glows* with red-heat until it is consumed. 4. Carbonization is, in general, best observed when the body is heated *rapidly* to a high temperature.]

§3. PUT A SMALL PORTION OF THE SUBSTANCE ON A CHARCOAL SUPPORT (IN THE CAVITY SCOOPED OUT FOR THE PURPOSE), AND EXPOSE TO THE INNER BLOWPIPE FLAME. 11

As most of the reactions described under 2 (3—10) are also produced by this process, I will here enumerate only those which result more particularly and exclusively from its application. Evolution of *sulphurous acid* in this experiment, usually denotes the presence of a metallic sulphide.

a. THE BODY FUSES, AND IS ABSORBED BY THE CHARCOAL OR FORMS A BEAD IN THE CAVITY without incrustation of the charcoal: this denotes more particularly the presence of salts of the alkalies. 12

b. AN INFUSIBLE WHITE RESIDUE REMAINS on the charcoal, either at once or after previous melting in the water of crystallization. This indicates more particularly the presence of baryta, strontia, lime, magnesia, alumina, oxide of zinc (which appears yellow whilst hot), and silicic acid. Among these substances, STRONTIA, LIME, MAGNESIA, and OXIDE OF ZINC, are distinguished by strong luminosity in the blowpipe flame. Moisten the white residue with a drop of solution of nitrate of protoxide of cobalt, and expose again to a strong heat. If the mass assumes a fine blue tint, this indicates the presence of ALUMINA; if a reddish tint, of MAGNESIA; if a green color, of OXIDE OF ZINC. If SILICIC ACID is present, the mass also assumes a faint bluish tint, which must not be confounded with that proceeding from the presence of alumina. 13

In cases *a.* and *b.* further examination may be made for the alkalies and alkaline earths by the flame-tests. A little of the substance is brought upon the loop of a fine platinum wire, moistened repeatedly with sulphuric acid, and cautiously dried near the edge of the gas flame, and finally brought into the zone of fusion. The alkalies first volatilize and tinge the flame; after they are dissipated, the baryta coloration, and lastly, on wetting with hydrochloric acid, the strontia and lime reactions appear. For details see § 95 and § 102.

c. THE SUBSTANCE LEAVES A RESIDUE OF ANOTHER COLOR, OR REDUCTION TO THE METALLIC STATE TAKES PLACE, OR THERE IS FORMED AN INCRUSTATION ON THE CHARCOAL. Mix a portion of the powder with carbonate of soda, and heat on charcoal in the reducing flame; observe the residue in the cavity, as well as the incrustation on the charcoal. 14

α. The sustained application of a strong flame produces a metallic globule, without incrustation of the charcoal; this indicates the presence of GOLD, or COPPER. The oxides of platinum, iron, cobalt, and nickel, are indeed also reduced, but they yield no metallic globules. 15

β. The charcoal support is coated with an incrustation, [illegible] with or without simultaneous formation of a metallic globule. 16

aa. The incrustation is *white*, at a long distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odor: ARSENIC.

bb. The incrustation is *white*, is nearer the test specimen than *aa*, and may be driven from one part of the support to another: ANTIMONY. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after the blowpipe jet is discontinued, and upon cooling may, if the metal is quite pure, become surrounded with crystals of teroxide of antimony; the globules are brittle.

cc. The incrustation is *yellow* whilst hot, but turns white on cooling; it is near the test specimen, and is with difficulty volatilized: ZINC.

dd. The incrustation has a *faint yellow* tint whilst hot, but turns white on cooling; it surrounds the test specimen, and both the inner and outer flame fail to volatilize it: TIN. The metallic globules formed at the same time (but only in a good reducing flame), are bright, readily fusible, and malleable.

ee. The incrustation has a *lemon-yellow* color, turning on cooling to sulphur yellow; when exposed to the reducing flame, it volatilizes tinging the flame azure-blue: LEAD. Readily fusible, malleable globules are formed at the same time with the incrustation.

ff. The incrustation is of a *dark orange-yellow* color whilst hot, which changes to lemon-yellow on

cooling; when exposed to the reducing flame, it changes its place without imparting any color to the flame: BISMUTH. The metallic globules formed at the same time as the incrustation are readily fusible and brittle.

gg. The incrustation is *reddish-brown*, in thin layers, orange-yellow; it volatilizes without tinging the flame: CADMIUM.

hh. The slight incrustation is *dark-red:* SILVER. In presence of a little lead or antimony it is crimson-red.

To learn, in cases of doubt, whether reduced metal has been separated in this experiment, the charcoal cavity is moistened with water, the charcoal cut out for a little space around and below the cavity, brought into an agate mortar, finely pulverized, and the charcoal powder cautiously washed away. Any metal that may be present remains in the mortar; gold in yellow, copper in red, silver in white, tin in grayish-white, lead in gray plates or streaks. Bismuth will remain as a reddish-gray, zinc a bluish-gray, antimony a gray powder. When copper and tin, or copper and zinc are simultaneously present, yellow alloys of these metals may be formed. [Iron, nickel and cobalt, when reduced on charcoal, remain after washing as black or dark-gray powders, which are lifted by the magnet.]

4. FUSE A SMALL PORTION TOGETHER WITH A BEAD OF MICROCOSMIC SALT, AND EXPOSE FOR SOME TIME TO THE OUTER FLAME OF THE BLOWPIPE. 17

a. THE SUBSTANCE DISSOLVES READILY AND RATHER LARGELY TO A CLEAR BEAD (WHILST HOT).

α. The hot bead is colored: 18

BLUE, by candlelight inclining to violet—COBALT;

GREEN, upon cooling blue; in the reducing flame, after cooling, red—COPPER;

GREEN, particularly fine on cooling, unaltered in the reducing flame—CHROMIUM;

BROWNISH-RED, on cooling light yellow or colorless; in the reducing flame red whilst hot, yellow whilst cooling, then greenish—IRON;

DARK YELLOW to REDDISH, turning lighter or altogether colorless on cooling; in the reducing flame unaltered—NICKEL;

YELLOWISH-BROWN, on cooling changing to light-

yellow or losing its color altogether; in the reducing flame almost colorless (especially after addition of a very little tin foil), blackish-gray on cooling—BISMUTH;

BRIGHT-YELLOWISH TO OPAL, when cold somewhat turbid; in the reducing flame whitish-gray—SILVER.

AMETHYST-RED, especially on cooling; colorless in the reducing flame, not quite clear—MANGANESE.

β. The hot bead is colorless: 19

IT REMAINS CLEAR ON COOLING: ANTIMONY, ALUMINA, ZINC, CADMIUM, LEAD, LIME, MAGNESIA; the latter five metals, when added in somewhat large proportion to the microcosmic salt, give enamel-white beads; the bead of oxide of lead is yellowish when saturated;

IT BECOMES ENAMEL-WHITE ON COOLING, even when only a small portion of the powder has been added to the microcosmic salt: BARYTA, STRONTIA.

b. THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY: 20

α. The bead is colorless, and remains so even after cooling; the undissolved portion looks semi-transparent; upon addition of a little sesquioxide of iron, it acquires the characteristic color of an iron bead: SILICIC acid.

β. The bead is colorless, and remains so after addition of a little sesquioxide of iron: TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD: GOLD, PLATINUM. 21

5. MINERALS SHOULD BE EXAMINED FOR FLUORINE according to § 149, 8.

As the body under examination may consist of a mixture of the most dissimilar elements, it is impossible to give well defined cases that shall offer at the same time the advantage of general applicability. If, therefore, reactions are observed in an experiment which proceed from a combination of two or several cases, the conclusions drawn from these reactions must of course be modified accordingly.

On concluding the Preliminary Examination, solution may be proceeded with according to § 183 (**32**).

§ 180.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. HEAT A SMALL PORTION OF THE SUBSTANCE WITH WATER ACIDULATED WITH ACETIC ACID. If HYDROGEN GAS is evolved this indicates the presence of a light metal (a metal of the 22

alkalies or alkaline earths), possibly also of metallic manganese.

2. HEAT A SAMPLE OF THE SUBSTANCE ON CHARCOAL IN THE REDUCING FLAME OF THE BLOWPIPE, and watch the reactions; for instance, whether the substance fuses, whether an incrustation is formed, or an odor emitted, &c. 23

In this operation the following metals may be detected with more or less certainty: ARSENIC by its garlic odor; MERCURY by its volatility: ANTIMONY, ZINC, LEAD, BISMUTH, CADMIUM, TIN and SILVER by their fusibility and yielding incrustations on the charcoal, compare (16), COPPER by its tinging the outer flame green; only when a single pure or nearly pure metal is present, is it possible to form further conclusions, thus GOLD is fusible without incrusting the charcoal; PLATINUM, IRON, MANGANESE, NICKEL and COBALT when pure are infusible.

3. HEAT A SAMPLE OF THE SUBSTANCE BEFORE THE BLOWPIPE IN A GLASS TUBE SEALED AT ONE END. 24

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OF THE TUBE: absence of mercury.

b. A SUBLIMATE IS FORMED; presence of MERCURY, CADMIUM, or ARSENIC. The sublimate of mercury, which consists of small globules, cannot possibly be confounded with that of cadmium or arsenic.

When the Preliminary Examination is finished, proceed to bring the substance into solution according to § 184 (42).

§ 181.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. EVAPORATE A SMALL PORTION OF THE FLUID IN A PLATINUM DISH, or in a small porcelain crucible, to ascertain whether it actually contains any matter in solution; if a residue remains, examine this as directed § 179. 25

2. TEST WITH LITMUS PAPER (blue and red). 26

a. THE FLUID REDDENS BLUE LITMUS PAPER. This reaction may be caused by a free acid or an acid salt, as well as by a metallic salt soluble in water. To distinguish between these two cases, pour a small quantity of the fluid into a watch-glass, and dip into it a small glass rod, the extreme point of which has previously been moistened with dilute solution of carbonate of soda; if the fluid remains clear, or if the precipitate which may form at first, redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt.

b. REDDENED LITMUS PAPER TURNS BLUE: this indicates 27

the presence of free alkalies or alkaline carbonates, free alkaline earths, alkaline sulphides, and of a number of other salts which contain an alkali or an alkaline earth in combination with a weak acid.

3. SMELL THE FLUID, or, should this fail to give satisfactory 28
results, DISTIL, to ascertain whether the simple solvent present is water, alcohol, ether, &c. If you find it is not water, evaporate the solution to dryness, and treat the residue as directed 179.

4. If the solution is aqueous, and manifests an acid reaction, 29
DILUTE A PORTION OF IT LARGELY WITH WATER. Should this impart a milky and turbid appearance to it, the presence of ANTIMONY, BISMUTH (possibly also of tin) may be inferred.

On completing the Preliminary Examination the operator 30
may proceed to the Actual Analysis. If the solution is aqueous and reacts neutral, only bodies which are soluble in water can be present; if, on the contrary, it has an acid reaction, which may be due to the presence of a free acid, it can no longer be considered simply aqueous, and the subsequent examination must accordingly be conducted with regard to the possible presence of substances insoluble in water but soluble in acids.

These circumstances being properly considered, the analyst passes over, when but *one acid* and *one base* are to be sought, to § 185 or to § 188—if *several acids or bases* are possibly present to § 192—solutions having an alkaline reaction are examined according to § 185 when containing but one acid and one base, otherwise according to § 192.

II. SOLUTION OF BODIES, OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOLVENTS *

§ 182.

Water, hydrochloric or nitric acid, and aqua regia are the 31
solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide the various substances into three classes, according to their respective behavior with these solvents.

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID OR AQUA REGIA.

Third class.—SUBSTANCES INSOLUBLE OR DIFFICULTLY

* Consult the remarks in the third section.

SOLUBLE IN WATER AS WELL AS IN HYDROCHLORIC ACID, NITRIC ACID, AND AQUA REGIA.

The solution of alloys being more appropriately effected in a different manner from that pursued with other bodies, I shall give a special method for these substances (see § 184).

The process of solution is conducted in the following manner.

A. The Substance under Examination is neither a Metal nor an Alloy.

§ 183.

1. Put about a gramme (15·5 grains) of the finely-pulverized substance under examination into a small flask or a test-tube, add from ten to twelve times the amount of distilled water, and heat to boiling over a spirit or gas-lamp. 32

a. The substance dissolves completely. In that case (regard being had to what has been stated in (30) concerning the reactions with test-papers), the substances may be reckoned in the first class. Treat the solution either as directed § 185, or as directed § 192, according as either one or several acids and bases are supposed to be present. 33

b. An insoluble residue remains, even after protracted boiling. Let the residue subside, and filter the fluid off, if practicable, in such a manner as to retain the residue in the test-tube; evaporate a few drops of the clear filtrate slowly on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed (35). But if a residue remains, the substance is at least partly soluble; in which case boil again with water, filter, add the filtrate to the original solution, and treat the fluid, according to circumstances, either as directed § 185, or according to § 192. Wash the residue with water, and proceed as directed (35). 34

2. Treat a small portion of the residue which has been boiled with water (34) with dilute hydrochloric acid. If it does not dissolve, heat to boiling, and if this fails to effect complete solution decant the fluid into another test-tube, boil the residue with concentrated hydrochloric acid, and if it dissolves, add it to the fluid in the other test-tube. The reactions which may manifest themselves in this operation, and which ought to be carefully observed are, (α) Effervescence, which indicates the presence of carbonic acid or hydrosulphuric acid; (β) Evolution of chlorine, which indicates the presence of peroxides, chromates, &c.; (γ) Emission of the odor of hydro- 35

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cyanic acid, which indicates the presence of insoluble cyanides. The analysis of the latter bodies being effected in a somewhat different manner, a special paragraph will be devoted to them (see § 207).

a. THE RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur separates, which may be known by its color and light specific gravity, and may, after boiling some time longer, be removed by filtration; or that gelatinous hydrate of silicic acid separates). Proceed, according to circumstances, either as directed § 188, or as directed § 193, after previous filtration if necessary. The body belongs to the second class. To make quite sure of the actual nature of the sulphur or hydrated silicic acid filtered off, examine these residuary matters as directed § 191, or as directed § 206. 36

b. THERE IS STILL A RESIDUE LEFT. In that case put aside the test-tube containing the specimen which has been boiled with the hydrochloric acid, and try and dissolve another sample of the substance under examination, or of the residue from the treatment with water, by boiling with nitric acid, and subsequent addition of water. In case binoxide of nitrogen or nitrous acid are evolved in this operation, it indicates that an oxidizing process is going on. 37

α. The sample is completely dissolved, or leaves no other residue but sulphur or the gelatinous hydrate of silicic acid; in this case also the body belongs to the second class. Use this solution to test further for bases, according to § 188, or, as the case may be (**109**), and for the rest proceed as directed in (**36**). 38

β. After boiling with nitric acid there is still a residue left. Pass on to (**40**). 39

3. If the residue insoluble in water will not entirely dissolve in hydrochloric acid or in nitric acid, try to effect complete solution of it by nitrohydrochloric acid. To this end mix the contents of the tube treated with nitric acid with the contents of the tube treated with concentrated hydrochloric acid; heat the mixture to boiling, and should this fail to effect complete solution, decant the clear fluid off from the undissolved residue, boil the latter for some time with concentrated nitrohydrochloric acid, and add the decanted solution in dilute aqua regia as well as the solution in dilute hydrochloric acid decanted in (**35**). Heat the entire mixture once more to boiling, and observe whether complete solution has now been effected, or whether the action of the concentrated nitrohydrochloric acid has still left a residue. In the *latter* case, filter the solu- 40

tion—if necessary, after addition of some water*—wash the residue with boiling water, and proceed with the filtrate, and the washings added to it, as directed § 188, or as directed § 193;—in the *former* case, proceed with the clear solution in the same way.†

4. If boiling nitro[illegible]rochloric acid has left an undissolved residue, wash it thoroughly with water, and then proceed as directed § 41, or as directed § 206. 41

B. The Substance under Examination is a Metal or an Alloy.

§ 184.

The metals are best classed according to their respective behavior with nitric acid: this gives us, 42

I. Metals which are not attacked by nitric acid: gold, platinum.

II Metals which are oxidized by nitric acid, but of which the oxides do not dissolve in an excess of the acid or in water: antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates, which dissolve in an excess of the acid or in water: all other metals.

Pour nitric acid of 1·20 sp. gr. over a small portion of the metal or alloy under examination, and apply heat.

1. Complete solution takes place, either at once or upon addition of water; this proves the absence of platinum,‡ gold, antimony,§ and tin. Proceed, according to circumstances, either as directed § 188, or as instructed § 192, III. (**109**). 43

2. A residue is left.

a. A metallic residue. Filter, and treat the filtrate as directed § 192, III., (**109**) after having examined, in the first place, whether anything has really been dissolved. 44

* If the fluid turns turbid upon addition of water, this indicates the presence of bismuth or antimony; the turbidity disappears again upon addition of hydrochloric acid.

† If the acid solution on cooling deposits acicular crystals, the latter generally consist of chloride of lead; it is in that case often advisable to decant the fluid off from the crystals, and to examine fluid and crystals separately. If on boiling with aqua regia, metabichloride of tin has been formed (by the action of the solvent on binoxide of tin), the wash waters, which dissolve it, will become turbid on falling into the acid solution which first passed the filter. In this case the two solutions are collected separately and separately treated with hydrosulphuric acid, according to § 193, both are however filtered afterwards through the same filter.

‡ Alloys of silver with a little platinum dissolve completely in nitric acid.

§ Very minute traces of antimony nevertheless often [illegible]s wholly into the solution.

Wash the residue thoroughly, dissolve in nitrohydrochloric acid, and examine the solution for GOLD and PLATINUM, according to § 131.

b. A white, pulverulent residue; this indicates the pre- 45
sence of ANTIMONY and TIN. Filter, ascertain whether anything has been dissolved, and treat the filtrate as directed § 192, III. (**109**). Wash the residue thoroughly, and examine according to § 137, 5, for ANTIMONY, TIN, and ARSENIC ACID (of which last a portion may exist in this residue, united to tin or antimony).

III. ACTUAL ANALYSIS.

*Simple Compounds.**

A. SUBSTANCES SOLUBLE IN WATER.

Detection of the Base.†

§ 185.

1. Add some hydrochloric acid to a portion of the aqueous 46
solution.

a. NO PRECIPITATE IS FORMED; this is a positive proof of the absence of silver and suboxide of mercury, and is likewise an indication of the probable absence of lead. Pass on to (**50**).

b. A PRECIPITATE IS FORMED. Divide the fluid in 47
which the precipitate is suspended into two portions, and add ammonia in excess to the one.

α. The precipitate redissolves, and the fluid becomes clear; this shows the precipitate to have consisted of chloride of silver, and is consequently indicative of the presence of SILVER. To arrive at a positive conviction on this point, the original solution must be tested with chromate of potassa, and with hydrosulphuric acid (see § 118, 4, and § 141, 6).

β. The precipitate turns black: this shows the pre- 48
cipitate to have consisted of subchloride of mercury, which has now been converted by the ammonia into

* This term is used here, and wherever it happens to occur hereafter in the present work, to designate compounds supposed to contain only *one* base and *one* acid, or *one* metal, and *one* non-metallic element.

This course of analysis of "simple compounds" is especially intended to facilitate the acquisition of a knowledge of the analytical method, it being on many accounts advantageous for the student to practise at first on bodies of simple composition before attempting to analyze complex substances. In other than analyses for mere practice, this course is only useful in a few exceptional cases, because there are no external indications which enable one to judge positively whether a body contains one or several acids or bases.

† Arsenious acid, arsenic acid, and silicic acid are included here.

subamidochloride of mercury; it is consequently indicative of the presence of SUBOXIDE OF MERCURY. To set all doubt on this point at rest, test the original solution with protochloride of tin, and with metallic copper (see § 119).

49 *γ. The precipitate remains unaltered;* it consists in that case of chloride of lead, which is not dissolved by ammonia; this reaction is accordingly indicative of the presence of LEAD. Whether the precipitate consists really of chloride of lead or not is conclusively ascertained: 1st, by diluting the second portion of the fluid in which the precipitate produced by hydrochloric acid is suspended, with a large amount of water, and applying heat; the precipitate must dissolve if it consists of chloride of lead; and 2nd, by adding dilute sulphuric acid to the original solution (§ 120, 8).

50 2. Add to the fluid acidified with hydrochloric acid (46) solution of hydrosulphuric acid until it smells distinctly of that gas, even after shaking; heat the mixture, add again some hydrosulphuric acid and let the whole stand a short time.*

α. THE FLUID REMAINS CLEAR. Pass on to (56), since this is a proof that lead, bismuth, copper, cadmium, oxide of mercury, gold, platinum, tin, antimony, arsenic, and sesquioxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

51 *α.* THIS PRECIPITATE IS WHITE; it consists in that case of separated sulphur, and is indicative of the presence of SESQUIOXIDE OF IRON (§ 114, 3). However, as the separation of sulphur may also be caused by other substances, it is indispensable that you should satisfy yourself whether the substance present is really sesquioxide of iron or not. For this purpose test the original solution with ammonia, and with ferrocyanide of potassium (§ 114, 5 and 6).

52 *β.* THE PRECIPITATE IS YELLOW; in that case it may consist either of sulphide of cadmium, sulphide of arsenic, or bisulphide of tin; it indicates accordingly the presence of either cadmium, arsenic, or binoxide of tin. To distinguish between these, mix a portion of the fluid wherein the precipitate is suspended with ammonia in excess, add some sulphide of ammonium, and heat.

* If a precipitate ensues immediately on addition of hydrosulphuric acid, shaking and repeated addition of the reagent are not needful. If, however, the fluid remains clear, or becomes but slightly turbid, the above directions must be closely followed or else *arsenic acid, binoxide of tin* and *oxide of mercury* may be overlooked.

aa. The precipitate does not dissolve; it consists of CADMIUM; for sulphide of cadmium is insoluble in ammonia and sulphide of ammonium. The blowpipe is resorted to as a confirmatory test (§ 125, 8).

bb. The Precipitate dissolves: BINOXIDE OF TIN OR ARSENIC; add ammonia to a small portion of the original solution.

aa. A white precipitate is formed. BINOXIDE OF TIN is the substance present. Positive conviction is obtained by reducing the precipitate before the blowpipe, with cyanide of potassium and carbonate of soda (§ 133, 8).

ββ. No precipitate is formed. This indicates the presence of ARSENIC. Positive conviction may be arrived at by the production of an arsenical mirror, which is effected by reducing the original substance or the precipitated sulphide of arsenic, either with cyanide of potassium and carbonate of soda, or in some other way; and moreover by exposing the original substance in conjunction with carbonate of soda to the inner flame of the blowpipe (§ 135, 12 and 13). If the solution (**50**) contained *arsenious* acid, the yellow precipitate (**52**) formed immediately upon the addition of the hydrosulphuric acid; if *arsenic* acid, it formed only upon the application of heat, or after long standing. For further information respecting the means of distinguishing between the two acids see § 137, 9.

γ. THE PRECIPITATE IS ORANGE-COLORED; in that case it consists of tersulphide of antimony, and indicates the **53** presence of TEROXIDE OF ANTIMONY. For confirmation, the original solution is tested with zinc in a small platinum dish (§ 134, 8).

δ. THE PRECIPITATE IS BROWN. It consists of proto- **54** sulphide of tin, and indicates the presence of PROTOXIDE OF TIN. To remove all doubt, test a portion of the original solution with solution of chloride of mercury (§ 132, 8).

ε. THE PRECIPITATE IS BROWNISH-BLACK OR BLACK. It **55** may in that case consist of sulphide of lead, sulphide of copper, tersulphide of bismuth, tersulphide of gold, bisulphide of platinum, or sulphide of mercury. To distinguish between these different sulphides, the following experiments are resorted to.

aa. Add dilute sulphuric acid to a portion of the

original solution; if a white precipitate is formed, this indicates LEAD. To dispel all doubt, test with chromate of potassa (§ 120).

bb. Add solution of soda to a portion of the original solution; if a yellow precipitate is formed, this indicates OXIDE OF MERCURY. The reactions with protochloride of tin and metallic copper, afford positive certainty on the point (§ 122).

The presence of oxide of mercury is usually sufficiently indicated by the several changes of color through which the precipitate produced by the solution of hydrosulphuric acid in the fluid under examination is observed to pass; this precipitate is white at first, but changes upon the addition of an excess of the precipitant to yellow, then to orange, and finally to black (§ 122, 3).

cc. Add ammonia in excess to a portion of the original solution; if a bluish precipitate is formed which redissolves in an excess of the precipitant, imparting an azure color to the fluid, this indicates COPPER. To remove all doubt, test with ferrocyanide of potassium (§ 123).

dd. If the precipitate produced by ammonia was white, and excess of ammonia has failed to redissolve it, filter the fluid off, wash the precipitate, dissolve it on a watch-glass in 1 or 2 drops of hydrochloric acid, with addition of 6 drops of water, and then add some more water. If the solution turns turbid and milky, this is caused by basic terchloride of bismuth: the reaction consequently indicates BISMUTH. The blowpipe is resorted to as a conclusive test (§ 124).

ee. Add solution of sulphate of protoxide of iron to a portion of the original solution. The formation of a fine black precipitate is indicative of the presence of GOLD. To remove all doubt as to the nature of the precipitate, expose it to the flame of the blowpipe, or test the original solution with protochloride of tin (§ 129).

ff. Add chloride of potassium and alcohol to a portion of the original solution; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. To remove all doubt, heat the precipitate to redness (§ 1

3. Mix a small portion of the original solution with chloride 56

of ammonium,* add ammonia to alkaline reaction, and then, no matter whether the latter reagent has produced a precipitate or not, a little sulphide of ammonium, and apply heat, if a precipitate fail to separate in the cold.

a. NO PRECIPITATE IS FORMED; pass on to (62); for iron, cobalt, nickel, manganese, zinc, chromium, alumina, and silicic acid, are not present.

b. A PRECIPITATE IS FORMED.

a. The precipitate is black: protoxide of iron, nickel, 57
or cobalt. Mix a portion of the original solution with some solution of potassa or soda.

aa. A dirty greenish-white precipitate is formed, which soon changes to reddish-brown, upon exposure to the air: PROTOXIDE OF IRON. To remove all doubt, test with ferricyanide of potassium (§ 113).

bb. A precipitate of a light greenish tint is produced, which does not change color: NICKEL. The reaction with ammonia, and the precipitation of the ammoniacal solution by potassa or soda, will afford positive certainty on the point (§ 111).

cc. A sky-blue precipitate is formed, which is discolored upon boiling, and acquires a dark tint: COBALT. The blowpipe is resorted to as a conclusive test (§ 112).

β. The precipitate is not black. 58

aa. If the precipitate is distinctly flesh-colored, it consists of sulphide of manganese, and is consequently indicative of the presence of PROTOXIDE OF MANGANESE. To remove all doubt, add soda to the original solution, or try before the blowpipe (§ 110).

bb. If the precipitate is bluish-green, it consists of hydrated sesquioxide of chromium, and is consequently indicative of the presence of SESQUIOXIDE OF CHROMIUM. To dispel all doubt, test the original solution with soda, and apply the blowpipe tests (§ 105).

cc. If the precipitate is white, it may consist of 59
hydrate of alumina, or hydrate of silicic acid, or sulphide of zinc, and may accordingly point to the presence of either alumina or oxide of zinc or silicic acid; the latter, in that case, is generally contained in the original solution as an alkaline silicate. To distinguish between these three bodies, add to a portion of

* The addition of chloride of ammonium is made to prevent the precipitation of *magnesia* by the ammonia.

the original solution, solution of soda drop by drop, wait to see whether this produces a precipitate, and then add some more solution of soda, until the precipitate formed is dissolved.

αα. If solution of soda fails to produce a precipitate, there is reason to test for SILICIC ACID. For that purpose, evaporate a portion of the original solution with hydrochloric acid to dryness, and treat the residue with hydrochloric acid and water (§ 153, 2), when the silicic acid will be left undissolved. Determine the nature of the alkali which has been dissolved, as directed (**66**). **60**

ββ. If solution of soda produces a precipitate, which redissolves in an excess of the precipitant, add to a portion of this alkaline fluid hydrosulphuric acid; the formation of a white precipitate indicates the presence of ZINC. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 109). If hydrosulphuric acid fails to produce a precipitate, add to the remaining portion of the alkaline fluid chloride of ammonium, and apply heat. The formation of a white precipitate indicates the presence of ALUMINA. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 104).

Note to (**58**), *and* (**59**).

As very slight contaminations may impair the distinctness of the tints exhibited by the precipitates considered in (**58**), and (**59**), it is advisable, in all cases where the least impurity is suspected, to adopt the following method for the detection of manganese, chromium, zinc, alumina, and silicic acid.

Add solution of soda to a portion of the original solution, first in small quantity, then in excess.

aa. No precipitate is formed: SILICIC ACID may be assumed to be present; proceed as directed (**60**). **61**

bb. A whitish precipitate is formed, which does not redissolve in an excess of the precipitant, and speedily turns blackish-brown upon exposure to the air MANGANESE. The blowpipe is resorted to as a conclusive test (§ 110).

cc. A precipitate is formed which redissolves in an excess of the precipitant: SESQUIOXIDE OF CHROMIUM, ALUMINA, OXIDE OF ZINC.

αα. Add hydrosulphuric acid water to a portion of

the alkaline solution. The formation of a white precipitate indicates the presence of ZINC.

$\beta\beta$. If the original or the alkaline solution is green, and if the precipitate produced by soda and redissolved by an excess of the precipitant, was of a bluish color, SESQUIOXIDE OF CHROMIUM is present. To remove all doubt, heat the alkaline solution to boiling, or try the reaction before the blowpipe (§ 105).

$\gamma\gamma$. Add chloride of ammonium to the alkaline solution. The formation of a white precipitate indicates the presence of ALUMINA. The reaction with solution of nitrate of protoxide of cobalt before the blowpipe will afford conclusive proof (§ 104).

4. Add to a portion of the original solution chloride of ammonium and carbonate of ammonia, mixed with some caustic ammonia, and heat gently. **62**

a. NO PRECIPITATE IS FORMED: absence of baryta, strontia, and lime. Pass on to (**64**).

b. A PRECIPITATE IS FORMED; presence of baryta, strontia, or lime. **63**

Add a considerable quantity of solution of sulphate of lime to a portion of the original solution.

a. *The solution does not become turbid, not even after the lapse of from five to ten minutes:* LIME. To remove all doubt, test with oxalate of ammonia (§ 100).

β. *The solution becomes turbid, but only after the lapse of some time:* STRONTIA.

This reaction is only conclusive when the solution is neutral or but slightly acid. The coloration of the flame is looked to for confirmation (§ 99, 6 or 7).

γ. *A precipitate is immediately formed:* BARYTA. To remove all doubt, test with hydrofluosilicic acid (§ 98).

5. Mix that portion of the solution of (**62**) in which carbonate of ammonia has, after previous addition of chloride of ammonium, failed to produce a precipitate, with phosphate of soda, add some more ammonia, and rub the sides of the vessel with a glass rod. **64**

a. NO PRECIPITATE IS FORMED: absence of magnesia. Pass on to (**65**).

b. A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. Evaporate a drop of the original solution on perfectly clean platinum foil as slowly as possible, and gently ignite the residue. **65**

a. THERE IS NO FIXED RESIDUE LEFT. Test for ammonia, by adding to the original solution hydrate of lime,

and observing the odor and reaction of the escaping gas, and the fumes which it forms with acetic acid (§ 94).

b. THERE IS A FIXED RESIDUE LEFT: potassa or soda. 66
Add bichloride of platinum to a portion of the original solution, having first concentrated it by evaporation if dilute, and shake the mixture.

α. No precipitate is formed, not even after the lapse of ten or fifteen minutes: SODA. The coloration of the flame is selected as a conclusive test, or the reaction with antimonate of potassa is resorted to for the purpose (§ 93).

β. A yellow crystalline precipitate is formed: POTASSA. The reaction with tartaric acid, and the coloration of the flame are selected as conclusive tests (§ 92).

Simple Compounds.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

I. *Detection of Inorganic Acids.*

§ 186.

Reflect in the first place *which* of the inorganic acids form soluble compounds with the detected base (compare Appendix IV.), and bear this in mind in your subsequent operations.

1. ARSENIOUS ACID and ARSENIC ACID have already been 67
considered in the preceding paragraph (detection of the base). These two acids are distinguished from each other by their respective behavior with nitrate of silver, or with potassa and sulphate of copper (see § 137, 9).

2. The presence of CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID, is also indicated already in the course of the process pursued for the detection of the bases. The two former betray their presence by effervescing upon the addition of hydrochloric acid; they may be distinguished from one another by their odor. Should additional proof be required, the presence of carbonic acid may be ascertained beyond a doubt by the reaction with lime-water (see § 152), and that of hydrosulphuric acid by the reaction with solution of acetate of lead (§ 159). The presence of chromic acid is invariably indicated by the yellow or red tint of the solution, as well as by the transition of the red or yellow color to green, accompanied by the separation of sulphur, upon the addition of hydrosulphuric acid water. To remove all doubt, try the reactions with solutions of acetate of lead and of nitrate of silver (§ 141).

3. A portion of the solution is slightly acidified with hydrochloric acid (or in case oxide of silver or protoxide of mercury has been detected, with nitric acid), and chloride of barium (or nitrate of baryta) is added.

a. THE FLUID REMAINS CLEAR. Absence of sulphuric acid. Pass on to (70),

b. A WHITE FINELY PULVERULENT PRECIPITATE IS FORMED. SULPHURIC ACID. The precipitate must remain undissolved on addition of more hydrochloric (or nitric) acid.

4. Add solution of sulphate of lime to another portion of the solution (which, if it has an acid reaction, must first be neutralized, or made slightly alkaline, by means of ammonia). 70

a. NO PRECIPITATE IS FORMED: absence of phosphoric acid, silicic acid, oxalic acid, and fluorine. Pass on to (73).

b. A PRECIPITATE IS FORMED. Add acetic acid in excess. 71

α. The precipitate redissolves readily: PHOSPHORIC ACID or SILICIC ACID. To a portion of the original solution hydrochloric acid is added in slight excess, the liquid is evaporated to dryness, and the residue treated with a little hydrochloric acid and water. If an insoluble residue remains it is SILICA. If no residue remains a portion of the original solution is mixed with chloride of ammonium, ammonia, and a little sulphate of magnesia. The formation of a crystalline precipitate is proof of the presence of PHOSPHORIC ACID (§ 145).

β. The precipitate remains undissolved or dissolves with difficulty: OXALIC ACID or FLUORINE. Oxalate of lime is pulverulent, fluoride of calcium flocculent and gelatinous. The reaction with binoxide of manganese and sulphuric acid (§ 148) will afford conclusive proof of the presence of oxalic acid; the reaction on glass (etching) of the presence of fluorine (§ 149). 72

5. Acidify a fresh portion of the original solution with nitric acid, and add solution of nitrate of silver. 73

a. THE FLUID REMAINS CLEAR. This is a proof of the absence of chlorine, bromine, iodine, ferrocyanogen, and ferricyanogen; the absence of cyanogen (in simple cyanides) is also probable. (Of the soluble metallic cyanides, cyanide of mercury is not precipitated by nitrate of silver; if, therefore, in the analytical process for the detection of the metals, mercury has been found, cyanide of mercury may be present. For the manner of detecting the cyanogen in the latter, see § 158, 8.) Pass on to (76).

[See § 136, 9, note.]

b. A PRECIPITATE IS FORMED.

α. The precipitate is orange colored: FERRICYANOGEN; 74
the reaction with sulphate of protoxide of iron is resorted to as a confirmatory test (§ 158, appendix).

β. The precipitate is white or yellowish-white. Treat the precipitate with ammonia in excess—at once, if the base be of the 1st or 2d groups—after filtering and washing if a base of the 3d or subsequent groups be present.

αα. The precipitate is not dissolved: IODINE or FERROCYANOGEN. In the former case the precipitate is pale-yellow, in the latter white and gelatinous. The reaction with starch and hyponitric acid (§ 157) will afford conclusive proof of the presence of iodine, the reaction with sesquichloride of iron of the presence of ferrocyanogen (§ 158, appendix).

ββ. The precipitate is dissolved: CHLORINE, BRO- 75
MINE, or CYANOGEN. If the original substance smells of hydrocyanic acid, and the silver precipitate dissolves with some difficulty in the ammonia, the precipitate may be assumed to consist of cyanide of silver, and, consequently, to indicate the presence of CYANOGEN. To remove all doubt on the point, add to the original solution sulphate of protoxide of iron, solution of soda, and hydrochloric acid (§ 158). If addition of chlorine water imparts a yellow tint to the original solution the precipitate may be held to consist of bromide of silver, and consequently indicates the presence of BROMINE; if the bromine is present only in very small proportion, chloroform or bisulphide of carbon must be used in conjunction with chlorine water to make the reaction distinctly apparent (§ 156). In the proved absence of both bromine and cyanogen, the precipitate consists of chloride of silver, and consequently shows the presence of CHLORINE.

6. Add to a small portion of the aqueous solution hydro- 76
chloric acid, drop by drop, until a distinct acid reaction is just imparted to the fluid, then dip in a slip of turmeric paper, take it out, and dry it at 212°. If the dipped portion looks brownish-red, BORACIC ACID is present. To settle all doubt on the point, add sulphuric acid and alcohol, and set fire to the latter (§ 147).

7. With regard to NITRIC ACID and CHLORIC ACID, these are 77
usually discovered already in the course of the preliminary examination (6). The reaction with sulphate of protoxide of

iron and sulphuric acid (§ 162) will afford conclusive evidence of the presence of the former, treatment of the solid salt with concentrated sulphuric acid, of the presence of the latter acid (§ 163).

Simple Compounds.

A. Substances soluble in Water. Detection of the Acid.

II. *Detection of Organic Acids.**

§ 187.

The analyst should in the first place ascertain by reference to the Index of solubilities (see Appendix IV.) what organic acids form soluble salts with the base which has been found in the substance under examination. Those which form insoluble salts, of course, cannot be present.

The following course implies that the organic acid is either in the free state or combined with an alkali or alkaline earth. If, therefore, any other base besides those belonging to groups I. and II. is present it must be removed. If the base belongs to the 5th or 6th groups it may be separated by hydrosulphuric acid; if it belongs to the 4th group, by sulphide of ammonium. After the metallic sulphide is filtered off, and excess of sulphide of ammonium is disposed of by acidulating with hydrochloric acid, warming and filtering off the sulphur, the clear liquid is examined according to (78). In case alumina or sesquioxide of chromium is the base present, the attempt should be made to throw it down by boiling with carbonate of soda. If this plan does not succeed, as will be the case when a non-volatile acid is present, the acid itself is precipitated by neutral acetate of lead, the precipitate is washed, diffused in a little water and hydrosulphuric acid gas passed through until the lead salt is decomposed. The sulphide of lead is filtered off and the filtrate examined according to (78). Alumina may also be thrown down from its combinations with non-volatile organic acids, by means of a solution of silicate of soda, in the form of a silicate of alumina.

1. Add ammonia to a portion of the aqueous solution of the compound under examination to *slight* alkaline reaction, then chloride of calcium. If the solution was neutral, or only 78

[* The indications of the preliminary examination (10 and note) are always sufficient to prove the presence or absence of an organic acid in "simple compounds." If, from inexperience, the operator is uncertain whether an organic acid be present, he will do well to go carefully through the following course, and then to repeat the preliminary examination (10), interpreting its results by the more positive proof of the actual analysis.]

slightly acid, add chloride of ammonium before adding the chloride of calcium.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER SHAKING THE FLUID NOR AFTER THE LAPSE OF A FEW MINUTES: absence of oxalic acid and tartaric acid.* Pass on to (**80**).

b. A PRECIPITATE IS FORMED. Add lime-water in excess to a fresh portion of the original solution, and then add solution of chloride of ammonium to the precipitate formed. **79**

α. The precipitate redissolves: TARTARIC ACID. The reaction with acetate of potassa may be resorted to as a confirmatory test; positive proof will also be afforded by the deportment which the precipitate produced by the chloride of calcium, and properly washed, exhibits with solution of soda or with ammonia and nitrate of silver (§ 166).

β. The precipitate does not redissolve: OXALIC ACID. To remove all doubt, try the reaction with concentrated sulphuric acid (§ 148).

2. Heat the fluid of 1, *a*, to boiling, keep at that temperature for some time, and add some more ammonia to the boiling fluid. **80**

a. IT REMAINS CLEAR: absence of citric acid. Pass on to (**81**).

b. IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID. To remove all doubt as to the nature of the acid, add solution of acetate of lead in excess, wash the precipitate formed, and see whether it dissolves readily in ammonia (§ 167).

3. Mix the fluid of 2, *a*, with alcohol. **81**

a. IT REMAINS CLEAR: absence of malic acid. Pass on to (**82**).

b. A PRECIPITATE IS FORMED: MALIC ACID. To remove all doubt, it is *invariably* necessary to try the reaction with acetate of lead, to see whether the precipitate produced by that reagent dissolves with difficulty in ammonia, and to examine its deportment when the fluid in which it is suspended is heated to boiling (§ 168).

4. Neutralize a portion of the original solution *exactly*† (if not

* [To be certain of the absence of tartaric acid, the solution must be concentrated.]

† [For this purpose, place a *very small* slip of blue litmus paper, and also one of red litmus or turmeric in the solution, and add, from the reagent bottle, either ammonia or hydrochloric acid, as is needed, *a single drop at a time*, agitating, to mix the liquids thoroughly, until the reagent is in excess. Then dilute a drop of the *other* reagent with enough water to fill a test-tube to the depth of half an inch, and apply this to the solution by means of a glass rod, until *it* is just in excess, when the point of neutralization is attained with sufficient accuracy.]

already absolutely neutral) with ammonia or with hydrochloric acid, and add solution of sesquichloride of iron. 82

a. A BULKY PRECIPITATE FORMS, OF A CINNAMON BROWN, OR DIRTY YELLOW COLOR. Wash the precipitate, heat it with ammonia, filter, concentrate the filtrate by evaporation to a small bulk, divide into two parts, and add to the one some hydrochloric acid, to the other alcohol and chloride of barium. The formation of a precipitate in the first portion indicates the presence of BENZOIC ACID, a precipitate in the second denotes the presence of SUCCINIC ACID. Compare § 171 and § 172.

b. THE LIQUID ACQUIRES A RATHER INTENSE DEEP RED TINT, AND, UPON PROTRACTED BOILING, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. Heat a portion of the solid salt under examination, or, if the substance is in the fluid state, of the residue left upon evaporating the fluid (which, if acid, you must neutralize first with soda), with sulphuric acid and alcohol (§ 174). The characteristic odor of acetic ether indicates the preesnce of ACETIC ACID. 83

If you do not detect acetic acid in the fluid, you may conclude that the substance under examination contains FORMIC ACID: to remove all doubt, try the reactions with nitrate of silver and chloride of mercury (§ 175).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

*Detection of the Base.**

§ 188.

Dilute a portion of the solution in hydrochloric acid, nitric acid, or nitrohydrochloric acid with water,† and proceed to examine for bases of the 2d, 5th, and 6th groups exactly as directed § 185, beginning at (**46**), in cases where the substance is dissolved in nitric acid, and at (**50**), if the solution already contains hydrochloric acid. 84

In testing for bases of the 3d and 4th groups by means of sulphide of ammonium according to (**56**) the usual course of

* Regard is also had here to certain salts of the alkaline earths, as this course of examination leads directly to their detection.

† If upon the addition of water the liquid becomes white and turbid or deposits a white precipitate, this indicates the presence of antimony or bismuth, possibly also of tin: compare § 124, 9, and 134, 4. Heat with hydrochloric acid until the fluid has become clear again, and then begin at (**50**).

analysis sometimes requires to be modified. Particular regard must therefore be had to the following observations: In cases where we have A SUBSTANCE SOLUBLE IN WATER, we obtain, in the course of the examination, a white precipitate upon adding chloride of ammonium, ammonia, and sulphide of ammonium; this precipitate can consist only of SULPHIDE OF ZINC, or ALUMINA, or HYDRATE OF SILICIC ACID as we have already seen (**59**). But the case is different if the body is INSOLUBLE IN WATER, but dissolves in hydrochloric acid; for in that case a white precipitate produced by sulphide of ammonium, in presence of chloride of ammonium, may consist also of PHOSPHATES, BORATES, OXALATES, SILICATES OF THE ALKALINE EARTHS, or of FLUORIDES OF THEIR METALS, as all these bodies are insoluble in water, but dissolve in hydrochloric acid, and (being only very sparingly soluble also in solution of chloride of ammonium) accordingly separate again upon neutralization of that acid. If, therefore, a white precipitate is produced upon testing an acid solution, under the circumstances stated, and according to the directions of § 185, (**56**) proceed as follows:—

1. If the results of the preliminary examination have given **85** you reason to suspect the presence of SILICIC ACID [**20**], evaporate a portion of the hydrochloric acid solution to dryness, moisten the residue with hydrochloric acid and add water. If silicic acid is present, it will remain undissolved. Determine the base in the solution as directed (**56**), or (**62**), as the case may require.

2. Add to a portion of the original hydrochloric acid solution, some tartaric acid, and after this ammonia in excess.

a. NO PERMANENT PRECIPITATE IS FORMED: absence of **86** the above enumerated salts of the alkaline earths. Mix another portion of the original solution with solution of soda in excess, and add to the one half of the clear fluid chloride of ammonium, to the other half hydrosulphuric acid. The formation of a precipitate in the former indicates the presence of ALUMINA; in the latter, the presence of ZINC.

b. A PERMANENT PRECIPITATE IS FORMED: presence of a salt of an alkaline earth.

α. A portion of the original substance is placed on a watch-glass, with a little binoxide of manganese, a few drops of water and some concentrated sulphuric acid. If evolution of carbonic acid forthwith takes place, the salt is an oxalate. Heat a sample of the original substance to redness, dissolve the residue in hydrochloric acid, and ascertain the nature of the alkaline earth in the solution as directed (**62**).

β. Add to a portion of the hydrochloric acid solution ammonia until a precipitate forms; then acetic acid until this is redissolved; lastly, acetate of soda and a drop of solution of sesquichloride of iron: the formation of a white flocculent precipitate indicates the presence of PHOSPHORIC ACID. Add now some more sesquichloride of iron until the fluid has acquired a distinct red color, boil, filter boiling, and test the filtrate, which is now free from phosphoric acid, for the alkaline earth with which the phosphoric acid was combined, as directed (62), after having previously removed, by precipitation with ammonia, the iron which may have been dissolved. 88

γ. Test a portion of the original substance, or of the precipitate produced in the hydrochloric acid solution by ammonia, with sulphuric acid for FLUORINE (§ 149). After removal of the fluorine, ascertain the nature of the alkaline earth now in the residue, combined with sulphuric acid (§ 191). 89

δ. BORACIC ACID is detected in the hydrochloric acid solution by means of turmeric paper (§ 147), and the base combined with it, by boiling a portion of the original substance with dilute solution of carbonate of soda, filtering, washing well the precipitated carbonate, dissolving it in the least possible quantity of dilute hydrochloric acid, and further proceeding with this solution according to (62).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACID.

I. *Detection of Inorganic Acids.*

§ 189.

1. CHLORIC ACID cannot be present, since all chlorates without exception are soluble in water; NITRIC ACID, which may be present in form of a basic salt, must have been revealed already by ignition of the body in a glass tube, and so must CYANOGEN (8). For the analysis of the metallic CYANIDES insoluble in water see § 207. The results of the test with phosphate of soda and ammonia will have directed attention to the presence of SILICIC ACID (20). Evaporation of the hydrochloric acid solution to dryness, and treatment of the residue 90

with hydrochloric acid and water will set all doubt at rest on the point (§ 153, 3).

2. The course of examination laid down here for the detec- **91** tion of the bases leads likewise to that of ARSENIOUS and ARSENIC ACIDS, CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID. With regard to the latter acid, I repeat that its presence is indicated by the yellow or red color of the compound, the evolution of chlorine which ensues upon boiling with hydrochloric acid, and the subsequent presence of sesquioxide of chromium in the solution. Fusion of the compound under examination with carbonate of soda is, however, the most conclusive test for chromic acid (§ 141).

3. Boil a portion of the substance with nitric acid. **92**

a. If nitric oxide gas is evolved, and sulphur separates, this is confirmative of the presence of a metallic sulphide.

b. If violet vapors escape, the compound is a metallic IODIDE.

c. If reddish-brown fumes of a chlorine-like smell are evolved, the compound is a metallic BROMIDE, in which case the fumes will color starch yellow (§ 156).

4. Dilute a portion of the solution obtained by boiling with **93** nitric acid (**92**)—or of the filtrate of this solution, should the nitric acid have left an undissolved residue—with water, and add solution of nitrate of silver to the fluid. The formation of a white precipitate which, after washing, is soluble in ammonia, and fuses without decomposition when heated, indicates the presence of CHLORINE.

5. Boil a portion of the substance with hydrochloric acid, **94** filter, if necessary, dilute with water, and add chloride of barium. The formation of a white precipitate, which does not redissolve even upon addition of a large quantity of water, indicates the presence of SULPHURIC ACID.

6. Test for BORACIC ACID as directed § 147, 6.

7. If none of the acids enumerated from 1 to 6 are present, **95** there is reason to suspect the presence of PHOSPHORIC ACID, OXALIC ACID, or FLUORINE, or the total absence of acids. To the presence of oxalic acid your attention will have been called already in the course of the preliminary examination (**8**). If the acids named had been combined with an alkaline earth, they would have already been detected in the course of the examination for these bases; they need therefore here be tested for, only in case the examination has revealed the presence of some other base. To that end, precipitate the base, according to circumstances, either with hydrosulphuric acid or with sulphide of ammonium and filter. If you have precipitated with sulphide of ammonium add to the filtrate hydro-

chloric acid to acid reaction, expel in either case the hydrosulphuric acid by boiling, and filter if necessary. Test a portion of this solution for phosphoric acid, oxalic acid, and fluorine, as directed (**70**). If the base is alumina or sesquioxide of chromium, *phosphoric acid* is tested by means of the nitric acid solution of molybdate of ammonia (§ 145, 10), *oxalic acid* with binoxide of manganese and oil of vitriol (§ 148), *fluorine* with oil of vitriol (§ 149).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN ACIDS.

DETECTION OF THE ACID.

II. *Detection of Organic Acids.**

§ 190.

1. FORMIC ACID cannot be present, as all the formates are **96** soluble in water.

2. ACETIC ACID has been revealed already in the course of the preliminary examination, by the disengagement of acetone. The reaction with sulphuric acid and alcohol (§ 174) will afford conclusive proof.

3. Boil a portion of the substance for some time with solution **97** of carbonate of soda in excess, and filter hot. You have now in most cases the organic acid in solution in combination with soda. Acidulate the solution slightly with hydrochloric acid, expel the carbonic acid by heat, and test as directed § 187. When a base of the 4th group, or oxide of lead is present, the separation by carbonate of soda is not complete. In such a case, after boiling with carbonate of soda, add to the filtrate sulphide of ammonium in slight excess, filter again and test the solution thus obtained.

Simple Compounds.

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND NITROHYDROCHLORIC ACID.

DETECTION OF THE BASE AND THE ACID.

§ 191.

Under this head we have to consider here, SULPHATE OF **98** BARYTA, SULPHATE OF STRONTIA, SULPHATE OF LIME, FLUORIDE OF CALCIUM, SILICA, SULPHATE OF LEAD, compounds of LEAD

* [See Note § 187.]

with CHLORINE and BROMINE, compounds of SILVER with CHLORINE, BROMINE, IODINE, and CYANOGEN, and lastly, SULPHUR and CARBON, as the only bodies belonging to this class which are more frequently met with. For the simple silicates I refer to § 208, for the ferro- and ferricyanides, to § 207. The preliminary examination will have informed you whether you need pay any regard to the possible presence of these compounds.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are so difficultly soluble that complete solution of them is seldom effected, they are included here also among the class of insoluble substances, to insure their detection, should they have been overlooked in the course of the examination of the aqueous or acid solution of the body to be analyzed.

1. Free SULPHUR must have been detected already in the course of the preliminary examination.

2. CARBON is usually black; it is insoluble in aqua regia; put on platinum foil, with the blowpipe flame playing upon the under side of the foil, it is always consumed; by deflagration with nitrate of potassa it yields carbonate of potassa.

3. Pour sulphide of ammonium over a very small quantity 99
of the substance under examination.

a. It TURNS BLACK; this indicates the presence of lead or a salt of silver.

α. The body fused in the glass tube without decomposition (3): chloride of lead, bromide of lead, chloride of silver, bromide of silver, iodide of silver. Fuse 1 part of the compound with 4 parts of carbonate of soda and potassa in a small porcelain crucible, let cool, boil the residue with water, and test the filtrate for CHLORINE, BROMINE, and IODINE, as directed (**73**). Dissolve the residue, which consists either of metallic SILVER or OXIDE OF LEAD, in nitric acid, and test the solution as directed (**46**).

β. The body evolved cyanogen, and left metallic silver behind: CYANIDE OF SILVER.

γ. The body remained unaltered: SULPHATE OF LEAD. Boil a sample of it with solution of carbonate of soda, filter, acidulate the filtrate with hydrochloric acid, and test with chloride of barium for SULPHURIC ACID; dissolve the washed residue in nitric acid, and test the solution with hydrosulphuric acid and with sulphuric acid for LEAD.

b. It REMAINS WHITE: absence of an oxide of a heavy 100

metal. A small sample is ground together with quartz sand, the mixture is placed on a watch-glass, moistened with a few drops of oil of vitriol and *gently* warmed.

α. *White vapors are evolved which redden litmus;* this indicates the presence of FLUORIDE OF CALCIUM. Reduce a portion of the substance to a fine powder, decompose this in a platinum crucible with sulphuric acid, and try the reaction on glass (§ 149), to prove the presence of FLUORINE; boil the residue with hydrochloric acid, filter, neutralize the filtrate with ammonia, and test for LIME with oxalate of ammonia.

β. *Vapors that redden litmus are not evolved.* Mix a small portion of the very finely pulverized substance with 4 times the quantity of pure carbonate of soda and potassa, and fuse the mixture in a platinum crucible, or else on platinum foil. Boil the fused mass with water, filter, should a residue be left, and wash the latter. Acidulate a portion of the filtrate with hydrochloric acid, and then test with chloride of barium for SULPHURIC ACID; and in case you do not find that acid, test another portion of the filtrate for SILICIC ACID by evaporating the fluid acidified with hydrochloric acid (§ 153, 2).

If the SILICIC ACID was present in the pure state, the mass resulting from the fusion of the substance with carbonate of soda and potassa must have dissolved in water to a clear fluid; but if silicates also happened to be present, their bases are left behind undissolved. and may be further examined.

If, on the other hand, sulphuric acid has been found, the alkaline earth which was combined with it is found on the filter as a carbonate. Wash this, then dissolve it in dilute hydrochloric acid, and test the solution for BARYTA, STRONTIA, and LIME, as directed (**62**).

*Complex Compounds.**

A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

* I use this term here. and hereafter in the present work, to designate compounds in which all the more frequently occurring bases, acids, metals, and metalloids are supposed to be present.

*Detection of the Bases.**

§ 192.†

(*Treatment with Hydrochloric Acid: Detection of Silver, Suboxide of Mercury* [*Lead*].)

The systematic course for the detection of the bases is essentially the same for bodies soluble in water, as for those which are soluble only in acids. Where, in consequence of the different nature of the original solution, deviations are rendered necessary, the fact will be distinctly stated. **101**

I. Solution in Water.

MIX THE PORTION INTENDED FOR THE DETECTION OF THE BASES WITH SOME HYDROCHLORIC ACID.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID. **102**

a. NO PRECIPITATE IS FORMED; this indicates the absence of silver and suboxide of mercury. Pass on to § 193.

b. A PRECIPITATE IS FORMED. Add more hydrochloric acid drop by drop until the precipitate ceases to increase; then add about six or eight drops more of hydrochloric acid, shake the mixture, and filter.

The precipitate produced by hydrochloric acid may consist of chloride of silver, subchloride of mercury, chloride of lead, a basic salt of antimony, basic oxychloride of bismuth, possibly also of benzoic acid. The basic salts of antimony and oxychloride of bismuth, however, redissolve in the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of chloride of silver, subchloride of mercury, or chloride of lead—(possibly also of benzoic acid, which, however, is altogether disregarded *here*).

Wash the precipitate collected upon the filter, twice with cold water, add the washings to the filtrate, and examine the solution as directed § 190, even though the addition of the washings to the acid filtrate should pro-

* The beginner should not fail to study the explanations in the Third Section thoroughly before attempting the analysis of a complex substance. He will also do well to review these explanations *frequently* during the course of his practice.

Regard is here had also to the presence of the acids of arsenic, and of those salts of the alkaline earths which dissolve in hydrochloric acid, and separate again from that solution unaltered, upon neutralization of the acid by ammonia.

† Consult the remarks in the Third Section.

duce turbidity in the fluid (which indicates the presence of compounds of antimony or bismuth).

Treat the washed precipitate on the filter as follows: 103

α. Pour hot water over it upon the filter, and test the fluid running off with sulphuric acid for LEAD. The non-formation of a precipitate upon the addition of the sulphuric acid simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid fails to precipitate lead from dilute solutions.

β. Pour over the now thrice-washed precipitate upon the filter, solution of ammonia. If this changes its color to black or gray, it is a proof of the presence of SUBOXIDE OF MERCURY.

γ. Add to the ammoniacal fluid running off in *β* nitric acid to strongly acid reaction. The formation of a white, curdy precipitate or opalescence indicates the presence of SILVER. (If the precipitate did contain lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic salt of lead. This, however, does not interfere with the testing for silver, since the basic salt of lead redissolves upon the addition of nitric acid.)

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION. 104

a. THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON FURTHER ADDITION OF HYDROCHLORIC ACID: pass on to § 193.

b. THE ADDITION OF HYDROCHLORIC ACID TO THE ORIGINAL SOLUTION PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.

a. The formation of the precipitate is attended neither with evolution of hydrosulphuric acid nor of hydrocyanic acid. Filter, and treat the filtrate as directed § 193. 105

aa. THE PRECIPITATE IS WHITE. It may, in that case, consist of a salt of lead or silver, insoluble in water and hydrochloric acid (CHLORIDE OF LEAD, SULPHATE OF LEAD, CHLORIDE OF SILVER, &c.) or may be HYDRATED SILICIC ACID. Test for the bases and acids of these compounds as directed § 206, bearing in mind that the chloride of lead or chloride of silver

which may be present may possibly have been formed in the process.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In that case it may consist of SULPHIDE OF ARSENIC (and if the fluid from which it has separated was not boiled for a long time, or only with very dilute hydrochloric acid, also of SULPHIDE OF ANTIMONY or BISULPHIDE OF TIN), which substances were originally dissolved in solution of ammonia, soda, potassa, phosphate of soda, or some other alkaline fluid, with the exception of solutions of alkaline sulphides and cyanides. Examine the precipitate which may also contain HYDRATED SILICA, as directed (**40**).

*β. The formation of the precipitate is attended with evolution of hydrosulphuric acid gas, but not of hydrocyanic acid.** **106**

aa. THE PRECIPITATE IS OF A PURE WHITE COLOR, AND CONSISTS OF SEPARATED SULPHUR. In that case a SULPHURETTED ALKALINE SULPHIDE is present. Boil, filter, proceed with the filtrate according to § 197, with the residue as directed § 206.

bb. THE PRECIPITATE IS COLORED. In that case you may conclude that a METALLIC SULPHUR SALT is present, *i. e.*, a combination of an alkaline sulphur base with a metallic sulphur acid. The precipitate may accordingly consist of SULPHIDE OF GOLD, SULPHIDE OF PLATINUM, SULPHIDE OF TIN, SULPHIDE OF ARSENIC, or SULPHIDE OF ANTIMONY. It might, however, consist also of SULPHIDE OF MERCURY or of SULPHIDE OF COPPER, or SULPHIDE OF NICKEL, or contain these substances, as the first is readily soluble in sulphide of potassium, and the last two are slightly soluble in sulphide of ammonium. Filter, and treat the filtrate according to § 197, the precipitate as directed (**40**).

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrosulphuric acid. This indicates the presence of an ALKALINE CYANIDE, and, if the evolution of the hydrocyanic acid is attended with that of hydrosulphuric acid, also of an alkaline SULPHIDE. In that case the precipitate may, besides **107**

* Should the odor of the evolved gas leave any doubt regarding the presence or absence of hydrocyanic acid, add some chromate of potassa to a portion of the fluid, previously to the addition of the hydrochloric acid.

the compounds enumerated in α (**105**) and β (**106**), contain many other substances (*e. g.*, cyanide of nickel, cyanide of silver, &c.). Boil, with further addition of hydrochloric acid, or of nitric acid, until the whole of the hydrocyanic acid is expelled, and treat the solution, or, if an undissolved residue has been left, the filtrate, as directed § 193; and the residue (if any) according to § 206.

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. **108**

α. *The escaping gas smells of hydrosulphuric acid;* this indicates the presence of a SIMPLE ALKALINE SULPHIDE. Proceed as in § 197.

β. *The escaping gas is inodorous;* in that case it is CARBONIC ACID which was combined with an alkali. Pass on to § 193.

γ. *The escaping gas smells of hydrocyanic acid* (no matter whether hydrosulphuric acid or carbonic acid is evolved at the same time or not). This indicates the presence of an ALKALINE CYANIDE. Boil until the whole of the hydrocyanic acid is expelled, and then pass on to § 193.

II. SOLUTION IN HYDROCHLORIC ACID OR IN NITROHYDROCHLORIC ACID.

Proceed as directed § 193.

III. SOLUTION IN NITRIC ACID.

Dilute a small sample of it with water; should this produce turbidity or a precipitate (indicative of the presence of bismuth) add nitric acid until the fluid is clear again, then hydrochloric acid. **109**

1. NO PRECIPITATE IS FORMED. Absence of silver and suboxide of mercury. Treat the principal solution as directed § 193.

2. A PRECIPITATE IS FORMED. Treat a larger portion of the nitric acid solution the same way as the sample, filter, and examine the precipitate as directed (**103**), the filtrate as directed § 193.

§ 193.*

(Treatment with Hydrosulphuric Acid, Precipitation of the Metallic Oxides of Group V. 2nd Section, and of Group VI.)

ADD TO A *small* PORTION OF THE CLEAR ACID SOLUTION HYDROSULPHURIC ACID WATER, UNTIL THE ODOR OF HYDROSULPHURIC ACID IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY.

1. NO PRECIPITATE IS FORMED, even after the lapse of some time. Pass on to § 197, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,† are not present;‡ the absence of sesquioxide of iron and of chromic acid is also indicated by this negative reaction. **110**

2. A PRECIPITATE IS FORMED.

a. The precipitate is of a pure white color, light and finely pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of SESQUIOXIDE OF IRON.§ None of the other metals enumerated in (**110**) can be present. Treat the principal solution as directed § 197. **111**

b. The precipitate is colored.

Add to the larger proportion of the acid or acidified solution, best in a small flask, hydrosulphuric acid water in excess, *i. e.*, until the fluid smells distinctly of it, and the precipitate ceases to increase upon continued addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the oxides present of Groups I.—IV.) for further examination, according to the instructions **112**

* Consult the remarks in the Third Section.

† Should the preliminary examination have led you to suspect the presence of arsenic acid, you must endeavor to obtain the most conclusive evidence of the absence of this acid; this may be done by allowing the fluid to stand for some time at a gentle heat (about 158° Fah.) or by heating it with sulphurous acid previous to the addition of the hydrosulphuric acid. (Compare § 136, 3.)

‡ In solutions containing much free acid, the precipitates are frequently formed only after dilution with water.

§ Sulphur will precipitate also if sulphurous acid, iodic acid, or bromic acid is present (which substances are not included in our analytical course), and also if chromic acid, chloric acid, or free chlorine is present. In presence of chromic acid, the separation of the sulphur is attended with reduction of the acid to sesquioxide of chromium, in consequence of which the reddish-yellow color of the solution changes to green. (Compare § 141.) The white sulphur suspended in the green solution looks at first like a green precipitate, which frequently tends to mislead beginners.

of § 197, and *thoroughly* wash (compare page 10) the precipitate which contains the sulphides of the metals present of Groups V. and VI.

In many cases, and more particularly when there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit hydrosulphuric acid gas through the solution DILUTED WITH WATER, instead of adding hydrosulphuric acid water.

If the precipitate is yellow, it consists principally 113
of sulphide of arsenic, sulphide of tin, or sulphide of cadmium; if orange-colored, this indicates sulphide of antimony; if brown or black, one at least of the following oxides is present: oxide of lead, teroxide of bismuth, oxide of copper, oxide of mercury, teroxide of gold, binoxide of platinum, protoxide of tin. However, as a yellow precipitate may contain small admixtures of an orange-colored, a brown, or even a black precipitate, and yet its color not be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in (**110**), in any precipitate produced by hydrosulphuric acid, and to proceed accordingly as the next paragraph directs.

§ 194.

(*Treatment of the Precipitate produced by Hydrosulphuric Acid with Sulphide of Ammonium; Separation of the 2nd Section of Group* V. *from Group* VI.)

INTRODUCE A SMALL PORTION OF THE (*thoroughly washed*) 114
PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID IN THE ACIDIFIED SOLUTION INTO A TEST-TUBE,* ADD A LITTLE WATER, AND TEN TO TWENTY DROPS OF YELLOW SULPHIDE OF AMMONIUM, AND EXPOSE THE MIXTURE FOR A SHORT TIME TO A GENTLE HEAT.†

* If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum or horn; but if you have only a very trifling precipitate, make a hole in the bottom of the filter, insert the perforated point into the mouth of the test-tube, rinse the precipitate into the latter by means of the washing-bottle, wait until the precipitate has subsided, and then decant the water.

† If the solution contains copper, which is generally revealed by the color of the fluid, and may be ascertained positively by testing with a clean iron rod (see § 123, 10), use solution of sulphide of sodium instead of sulphide of ammonium (in which sulphide of copper is not absolutely insoluble, see § 123, 5), and boil the mix-

1. THE PRECIPITATE DISSOLVES COMPLETELY IN SULPHIDE OF AMMONIUM (or SULPHIDE OF SODIUM, as the case may be): absence of the metals of Group V.—cadmium, lead, bismuth, copper, mercury. Treat the remainder of the precipitate (of which you have digested a portion with sulphide of ammonium) as directed § 195.—If the precipitate produced by hydrosulphuric acid was so trifling that you have used the whole of it in treating with sulphide of ammonium, precipitate the solution obtained in that process by addition of hydrochloric acid, filter, wash the precipitate, and treat the latter as directed § 195. **115**

2. THE PRECIPITATE IS NOT REDISSOLVED, OR AT LEAST NOT COMPLETELY: presence of the metals of Group V. **116**

Dilute with 4 or 5 parts of water, filter, and mix the filtrate with hydrochloric acid in slight excess.

a. The fluid simply turns milky, owing to the separation of sulphur. Absence of the metals of Group VI.—gold, platinum, tin, antimony, and arsenic.* Treat the rest of the precipitate (of which you have digested a portion with sulphide of ammonium), according to the directions of § 196.

b. A colored precipitate is formed: presence of metals of Group VI. by the side of those of Group V. Treat the entire precipitate produced by hydrosulphuric acid the same as you have treated a portion of it, *i. e.*, digest it with yellow sulphide of ammonium, or, as the case may be, sulphide of sodium, let it subside, pour the supernatant liquid on a filter, digest the residue in the tube once more with yellow sulphide of ammonium (or **117**

ture. But if the fluid, besides copper, also contains oxide of mercury (the presence of which is generally sufficiently indicated by the several changes of color exhibited by the precipitate forming upon the addition of the hydrosulphuric acid (§ 122, 3), and which, in doubtful cases, may be detected with positive certainty by testing a portion of the original solution acidified with hydrochloric acid, with protochloride of tin, sulphide of ammonium must be used, although the separation of the sulphides of the antimony group from the sulphide of copper is not fully effected in such cases; since, were sulphide of sodium used, the sulphide of mercury would dissolve in this reagent, and this would impede the ulterior examination of the sulphides of the antimony group. [If the mixture is *heated to boiling* before filtering off, sulphide of ammonium may be used in all cases, only the very minutest traces of copper, or none at all being dissolved.—*Editor.*]

* That this inference becomes uncertain if the precipitate produced by hydrosulphuric acid, instead of being digested with a small quantity of sulphide of ammonium, has been treated with a larger quantity of that reagent, is self-evident; for the large quantity of sulphur which separates in that case will, of course, completely conceal any slight traces of sulphide of arsenic or bisulphide of tin which may have been thrown down. In case of doubt, proceed according to (**117**).

sulphide of sodium), and filter. Wash the residue* (containing the sulphides of Group V.), and treat it afterwards as directed § 196. Dilute the filtrate—which contains the metals of Group VI. in the form of sulphur salts—with water, add hydrochloric acid to slightly acid reaction, heat gently, filter the precipitate formed—which contains the sulphides of the metals of Group VI. mixed with sulphur—*wash thoroughly*, and proceed as directed next paragraph (§ 195).

§ 195.

(*Detection of the Metals of Group* VI.: *Arsenic, Antimony, Tin, Gold, Platinum.*)

If the precipitate consisting of the sulphides of Group VI. has a PURE YELLOW COLOR, this indicates principally arsenic and tin; if it is distinctly ORANGE-YELLOW, antimony is present; if it is BROWN or BLACK, this denotes the presence of platinum or gold. 118

Beyond these general indications, the color of the precipitate affords no safe guidance. It is therefore always advisable to test yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely hid by a large quantity of bisulphide of tin or tersulphide of arsenic. Proceed accordingly as follows:

Heat a little of the precipitate on the lid of a porcelain crucible, or on a fragment of porcelain or glass.†

1. *Complete volatilization ensues:* probably presence of ARSENIC, absence of the other metals of Group VI. Reduction of a portion of the precipitate with cyanide of potassium and carbonate of soda (§ 135, 12)‡ will 119

* If the residue suspended in the fluid containing sulphide of ammonium, and insoluble therein, subsides readily, it is not transferred to the filter, but washed in the tube by decantation. But if its subsidence proceeds slowly and with difficulty it is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a washing bottle; the application of a gentle heat will materially aid the subsidence of the residue, and the supernatant water may then be decanted. Sometimes the suspended sulphides are so finely divided as to run through the filter. In such a case add to the liquid a little chloride of ammonium.

† That this preliminary examination may be omitted if the precipitate is not yellow, and that it can give a decisive result only if the sulphur precipitate submitted to the test has been *thoroughly washed*, is self-evident.

‡ If the precipitate contains much free sulphur, it is digested for some time with ammonia, which dissolves the tersulphide of arsenic. The filtered solution is evaporated to dryness at a gentle heat with addition of a little carbonate of soda, and this residue is heated with cyanide of potassium and soda as above directed.

afford positive proof of the presence or absence of arsenic. Whether that metal was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the method described § 137, 9.

2. *A fixed residue is left.* In that case all the metals 190
of Group VI. must be sought for. Dry the remainder of the precipitate thoroughly upon the filter, triturate it together with about 1 part of anhydrous carbonate of soda and 1 part of nitrate of soda, and transfer the mixture in small portions at a time to a small porcelain crucible, in which you have previously heated 2 parts of nitrate of soda to fusion.* As soon as complete oxidation is effected, pour the mass out on a piece of porcelain.

After cooling, soak the fused mass (the portion still sticking to the inside of the crucible as well as the portion poured out on the porcelain) in cold water, filter the insoluble residue—which will remain if the mass contained antimony, tin, gold, or platinum—and wash well with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the solution of the antimonate of soda. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

a. EXAMINATION OF THE FILTRATE FOR ARSENIC 191
(which must be present in it in the form of arsenate of soda).

To the filtrate add nitric acid [illegible]utiously to faint acid reaction,† heat to expel carbon[illegible]nd nitrous acids, and then divide the liquid into two portions.—To one portion add some nitrate of silver (if too little), filter.

* Should the amount of the precipitate be so minute that this operation cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these together with some carbonate of soda and nitrate of soda, and project both the powder and the paper into the fusing nitrate of soda. It is *preferable*, however, in such cases, to procure at once, if practicable, a sufficiently large amount of the precipitate, as otherwise there will be but little hope of effecting the positive detection of all the metals of Group VI. Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of antimonate and arsenate of soda, binoxide of tin, metallic gold and platinum, sulphate, carbonate, nitrate, and some nitrite of soda. Compare also § 137, 1.

† In some cases where a somewhat larger proportion of carbonate of soda had been used, or a very strong heat applied, a trifling precipitate (hydrated binoxide of tin) may separate upon the acidification of the filtrate with nitric acid. This may be filtered off, and then treated in the same manner as the undissolved residue.

(in case some chloride of silver* or nitrite of silver should have separated), pour upon the filtrate, along the side of the tube held slanting, a layer of dilute solution of ammonia,—2 parts of water to 1 part of solution of ammonia—and let the mixture stand for some time without shaking. The formation of a reddish-brown precipitate, which floats cloud-like between the two layers (and may be seen far more readily and distinctly by reflected than by transmitted light), denotes the presence of ARSENIC.

If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, the fluid being stirred during this process, the precipitate of arsenate of silver which forms imparts a brownish-red tint to the entire fluid.

To the other portion of this acidified solution, add **122** ammonia, then a mixture of sulphate of magnesia and chloride of ammonium† and rub the sides of the test-tube with a glass rod. The formation of the crystalline precipitate of arsenate of ammonia-magnesia, which often forms only after the lapse of some time and especially on the sides of the tube, is further evidence of the presence of arsenic. For additional confirmation the arsenic may be procured in the metallic state. (Compare § 135 and § 136.)

Whether the arsenic was present in the form of arsenious acid or in that of arsenic acid, may be ascertained by the method described, § 137, 9.

b. EXAMINATION OF THE RESIDUE FOR ANTIMONY, TIN, **123** GOLD, PLATINUM. (As the antimony, if present in the residue, must exist as white, pulverulent antimonate of soda, the tin as white, flocculent binoxide, the gold and platinum in the metallic state, the appearance of the residue is in itself indicative of its nature.) The precipitate is placed in a small vessel of platinum [or in a porcelain dish in contact with a slip of platinum foil] and heated with a little hydrochloric acid. Water is now added, and (disregarding any undissolved residue) a compact piece of pure (lead-free) zinc is put into the liquid. Gold and platinum, through all these operations, from the fusion forward, exist in the metallic state. Tin and antimony are now reduced to the metallic state by

* Chloride of silver will separate if the reagents were not perfectly pure, and the precipitate has not been thoroughly washed.

† [See § 136, 9, note.]

the zinc. ANTIMONY is however at once, or shortly, recognized by the black stain it produces on the platinum. As soon as hydrogen gas has nearly ceased to escape, what remains of the zinc is removed, the liquid—a solution of chloride of zinc—is carefully poured off, and the residual metals are warmed with hydrochloric acid. In the solution thus prepared, which, if TIN be present, contains protochloride of tin, this metal is tested by means of chloride of mercury (§ 132, 8).

The contents of the platinum vessel (**123**) are freed **124**
from tin by repeatedly boiling with hydrochloric acid, and in case an insoluble residue is left—the acid is also removed by washing it with water. The residue is then examined in the following manner: It is warmed in the platinum dish with some water and a little tartaric acid, and lastly with addition of a few drops of nitric acid. If it dissolves completely, gold and platinum are not present; if an insoluble residue remains these metals must be looked for.

The acid solution is decanted (in it the presence of ANTIMONY may be confirmed by hydrosulphuric acid), the residue is washed several times by decantation, *transferred to a porcelain dish* and dissolved by aid of a little nitrohydrochloric acid. The solution is evaporated to a very small bulk and further tested as directed § 131 for GOLD and PLATINUM.

§ 196.

(Detection of the Metallic Oxides of Group V. 2d Section:—Oxide of Lead. Teroxide of Bismuth. Oxide of Copper. Oxide of Cadmium. Oxide of Mercury.

THOROUGHLY WASH THE PRECIPITATE WHICH HAS NOT BEEN **125**
DISSOLVED BY SULPHATE OF AMMONIUM, AND BOIL WITH NITRIC ACID. This operation is performed best in a small porcelain dish; the boiling mass must be constantly stirred with a glass rod during the process. A great excess of acid must be avoided.

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS FLOAT- **126**
ING IN THE FLUID ONLY THE SEPARATED, LIGHT, FLOCCULENT, YELLOW SULPHUR; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH may be present.

Filter the fluid from the separated sulphur, and treat the filtrate as follows (should there be too much nitric acid present, the greater part of this must first be driven off by evaporation): add to a portion of the filtrate dilute sulphuric

acid in moderate quantity, heat gently, and let the fluid stand some time.

a. NO PRECIPITATE FORMS; absence of lead. Mix the remainder of the filtrate with ammonia in excess, and gently heat. **127**

α. No precipitate is formed; absence of BISMUTH. If the liquid is blue, COPPER is present; very minute traces of copper, however, might be overlooked, if the color of the ammoniated fluid alone were consulted. To be quite safe, and also to test for cadmium, evaporate the ammoniated solution nearly to dryness, add a little acetic acid, and, if necessary, some water, and **128**

aa. Test a small portion of the fluid for copper with ferrocyanide of potassium. The formation of a reddish-brown precipitate, or a light brownish-red turbidity, indicates the presence of COPPER (in the latter case only to a very trifling amount). **129**

bb. Mix the remainder of the fluid with solution of hydrosulphuric acid in excess. The formation of a yellow precipitate denotes CADMIUM. If, on account of the presence of copper, the sulphide of cadmium cannot be distinctly recognised, allow the precipitate produced by the hydrosulphuric acid to subside, decant the supernatant fluid, and add to the precipitate solution of cyanide of potassium until the sulphide of copper is dissolved. If a yellow residue is left undissolved, CADMIUM is present; in the contrary case, not. **130**

β. A precipitate is formed. BISMUTH is present. Filter the fluid, and test the filtrate for copper and cadmium, as directed in α (**128**). To test the washed precipitate more fully for bismuth, dry the filter containing it somewhat between blotting-paper, remove the still moist precipitate with a platinum spatula, dissolve in a watch-glass in the *least possible quantity* of hydrochloric acid, and then add a considerable quantity of water. The appearance of a milky turbidity confirms the presence of bismuth. **131**

b. A PRECIPITATE IS FORMED. Presence of LEAD. Bring the entire nitric solution into a porcelain capsule, add enough dilute sulphuric acid to form sulphate with the lead, and evaporate in the water-bath until all nitric acid is expelled, add to the residue a little water mixed with dilute sulphuric acid, filter off immediately from the insoluble sulphate of lead, and examine the filtrate for bis- **132**

muth, copper, and cadmium, as directed in *a* (**127**).* Test the precipitate, after washing, by one of the methods described in § 126.

2. THE PRECIPITATE OF THE METALLIC SULPHIDES DOES NOT COMPLETELY DISSOLVE IN THE BOILING NITRIC ACID, BUT LEAVES A RESIDUE, BESIDES THE SULPHUR THAT FLOATS IN THE FLUID. **133**

Probable presence of OXIDE OF MERCURY (which may be pronounced almost certain, if the precipitate is heavy and black). Allow the precipitate to subside, filter off the fluid, which must still be tested for CADMIUM, COPPER, LEAD, and BISMUTH; mix a small portion of the filtrate with a large amount of solution of hydrosulphuric acid, and should a precipitate form or a coloration become visible, treat the remainder according to the directions of (**126**).

Wash the residue (which, besides sulphide of mercury, may also contain sulphate of lead, (formed by the action of nitric acid upon sulphide of lead), and also binoxide of tin, and possibly sulphides of gold and platinum, as the complete separation of these sulphides from the sulphides of the metals of Group V. is rather difficult), and examine one half of it for mercury,† by dissolving it in some hydrochloric acid, with addition of a very small proportion of chlorate of potassa, and testing the solution with copper, or protochloride of tin (§ 122); fuse the other half with cyanide of potassium and carbonate of soda. If on treating the fused mass with water, you obtain metallic grains or a metallic powder, wash, heat with nitric acid, and test the solution obtained, with sulphuric acid for lead. If nitric acid leaves a residue, this is washed and any hydrated metastannic acid it may contain is extracted from it in the form of metabichloride of tin by boiling for a time with hydrochloric acid, pouring off the acid and adding water (see § 133, 1).

If a heavy metallic powder remains after this treatment it is dissolved in aqua regia and the solution tested for gold and platinum according to § 131.

§ 197.

(*Precipitation with Sulphide of Ammonium, Separation and Detection of the Oxides of Groups* III. *and* IV.: *Alumina, Sesquioxide of Chromium;—Oxide of Zinc, Protoxide of Man-*

* For another method of distinguishing cadmium, copper, lead, and bismuth from each other, I refer to the Third Section (additions and remarks to § 196).

† If you have an aqueous solution, or a solution in very dilute hydrochloric acid, the oxide of mercury formed was present in the original substance in that form; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid, the mercury may most likely have been originally present in the form of suboxide, and may have been converted into oxide in the process.

ganese, Protoxide of Nickel, Protoxide of Cobalt, Proto- and Sesquioxide of Iron; and also of those Salts of the Alkaline Earths which are precipitated by Ammonia from their Solution in Hydrochloric Acid; Phosphates, Borates, Oxalates, Silicates and Fluorides.)

PUT A *small portion* OF THE FLUID IN WHICH SOLUTION OF HYDROSULPHURIC ACID HAS FAILED TO PRODUCE A PRECIPITATE (**110**) OR OF THE FLUID WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED (**112**) in a test tube, observe whether it is colored or not,* boil to expel the hydrosulphuric acid which may be present, add a few drops of nitric acid, boil, and observe again the color of the fluid; then cautiously add ammonia to alkaline reaction, observe whether this produces a precipitate, and then add some sulphide of ammonium, no matter whether ammonia has produced a precipitate or not. **134**

a. NEITHER AMMONIA NOR SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE. Pass on to § 198, for iron, nickel, cobalt, zinc, manganese, sesquioxide of chromium, alumina, are not present, nor are phosphates, borates,† silicates, and oxalates‡ of the alkaline earths; nor fluorides of the metals of the alkaline earths; nor silicic acid originally united to alkalies. **135**

b. SULPHIDE OF AMMONIUM PRODUCES A PRECIPITATE, AMMONIA HAVING FAILED TO DO SO; absence of phosphates, borates,† silicates, and oxalates‡ of the alkaline earths; of the fluorides of the metals of the alkaline earths; of silica originally united to alkalies, and also, if no organic matters are present, of iron, sesquioxide of chromium, and alumina. Pass on to (**138**). **136**

c. AMMONIA PRODUCES A PRECIPITATE before the addition of sulphide of ammonium. The course of proceeding to be pursued now depends upon whether (*α*) the original solution is simply aqueous, and has a neutral **137**

* If the fluid is colorless, it contains no chromium or but a very minute quantity. If colored, the tint will to some extent act as a guide to the nature of the substance present; thus a green tint, or a violet tint turning green upon boiling, points to the presence of chromium; a light green tint to that of nickel; a reddish color to that of cobalt; the turning yellow of the fluid upon boiling with nitric acid, to that of iron. It must, however, be always borne in mind that these tints are perceptible only if the metallic oxides are present in larger quantity, and also that complementary colors, such as, for instance, the green of the nickel solution and the red of the cobalt solution, will destroy each other, and that, accordingly, a solution may contain both metals and yet appear colorless.

† Presence of much chloride of ammonium has a great tendency to prevent the precipitation of borates of the alkaline earths.

‡ Oxalate of magnesia is thrown down from hydrochloric solution by ammonia only after the lapse of some time, and never completely: dilute solutions are not precipitated at all.

reaction, or (β) the original solution is acid or alkaline. In the former case, pass on to (**138**), for phosphates, borates, oxalates, and silicates of the alkaline earths cannot be present; nor can fluorides of the metals of the alkaline earths nor silica in combination with alkalies. In the latter case, regard must be had to the possible presence of all the bodies enumerated in (**135**); pass on to (**150**).

1. DETECTION OF THE BASES OF GROUPS III. AND IV. IF PHOSPHATES, &C., OF THE ALKALINE EARTHS ARE NOT PRESENT.* **138**

Mix the fluid mentioned at the beginning of the paragraph (**134**) (a portion of which you have submitted to a preliminary examination) with some chloride of ammonium, then with ammonia, just to alkaline reaction; lastly, with sulphide of ammonium, until the fluid, after being shaken, smells distinctly of that reagent; shake the mixture until the precipitate begins to separate in flocks, warm gently for a time, and filter.

Keep the FILTRATE,† which contains, or may contain, the bases of Groups II. and I., for subsequent examination according to the directions of § 198. Wash the PRECIPITATE with water, to which a very little sulphide of ammonium has been added, and then proceed with it as follows:—

a. IT IS PERFECTLY WHITE; absence of iron, cobalt, nickel. You must test for all the other bases of Groups III. and IV., as the faint tints of sesquioxide of chromium and sulphide of manganese are imperceptible in a large quantity of a white precipitate. Dissolve the precipitate by heating it in a small dish with the least possible amount of hydrochloric acid; boil—should hydrosulphuric acid be evolved—until this gas is completely expelled, concentrate by evaporation to a small bulk, neutralize with carbonate of soda, then add solution of soda in excess, heat to boiling, and keep the mixture for some time in a state of ebullition. **139**

a. *The precipitate formed at first dissolves completely in the excess of solution of soda.* Absence of manganese and chromium, presence of alumina or oxide of zinc. Test a portion of the alkaline solution with solu- **140**

* This simpler course is quite good enough for most purposes; in very accurate analyses, however, the course beginning at (**150**) is to be followed, since it leads to the detection of the traces of alkaline earths which are thrown down with alumina and sesquioxide of chromium.

† If the filtrate has a brownish color, this points to the presence of nickel, sulphide of nickel, as is well known, being slightly soluble in sulphide of ammonium this, however, involves no modification of the analytical course.

tion of hydrosulphuric acid for ZINC; acidify the remainder with hydrochloric acid, add ammonia *slightly* in excess, and apply heat. The formation of a white, flocculent precipitate shows the presence of ALUMINA.

β. The precipitate formed does not dissolve, or dissolves only partially, in the excess of solution of soda. 141
Filter and test the FILTRATE, as in *α* (140), for ZINC and ALUMINA. With the undissolved PRECIPITATE which, when much manganese is present, has a brown or brownish color, proceed as follows:—

aa. Should the color of the solution indicate the absence of chromium, test a portion of the precipitate for MANGANESE by means of the reaction with carbonate of soda in the outer blowpipe flame.

bb. If chromium is indicated by the color of the 142
solution, the examination of the residue insoluble in solution of soda becomes more complicated, since it may contain zinc, and indeed, perhaps all the zinc of the original substance (§ 115). The precipitate is dissolved in hydrochloric acid, the solution is evaporated to a small bulk, diluted, the free acid nearly neutralized by means of carbonate of soda, a slight excess of carbonate of baryta added, and the whole digested in the cold with occasional agitation until the solution has become colorless. It is now filtered and the precipitate is tested for chromium by fusion with carbonate of soda and nitrate of soda or potassa (§ 105, 8). The solution is treated hot with excess of dilute sulphuric acid and filtered, to remove baryta, the filtrate is evaporated to a small volume and supersaturated with strong solution of soda. If any precipitate is formed, it is filtered off and tested as in *aa.* for MANGANESE; the filtrate is examined for ZINC with hydrosulphuric acid.

b. IT IS NOT WHITE; this points to the presence of chro- 143
mium, manganese, iron, cobalt, or nickel. If it is black, or inclines to black, one of the three metals last mentioned is present. Under all circumstances, all the oxides of Groups III. and IV. must be looked for.

Remove the washed precipitate from the filter with a spatula, or by rinsing it, with the aid of a washing-bottle, into a test-tube, through a hole made in the bottom of the filter, and pour over it rather dilute cold hydrochloric acid in moderate excess.

α. It dissolves completely (except perhaps a little 144

sulphur, which may separate); absence of cobalt and nickel, at least of notable quantities of these two metals.

Boil until the hydrosulphuric acid is *completely* expelled, filter if particles of sulphur are suspended in the fluid, concentrate by evaporation to a small volume, then add solution of potassa or soda in excess, boil, filter the fluid from the insoluble precipitate which is sure to remain, wash the latter, and proceed first to examine the filtrate, then the precipitate.

aa. Test a portion of the *filtrate* with hydrosulphuric acid for *zinc*; acidify the remainder with hydrochloric acid, and then test it with ammonia for ALUMINA. Compare (140). 145

bb. Dissolve a portion of the *precipitate* in hydrochloric acid, and test the solution with sulphocyanide of potassium for IRON. Test another portion for CHROMIUM by fusing it with carbonate and nitrate of soda (§ 105, 8). If chromium is not thus detected, the remainder of the precipitate is examined with carbonate of soda in the oxidizing flame for MANGANESE. If, on the contrary, chromium is present, the remainder of the precipitate, which may in that case contain manganese and zinc and indeed the whole of the latter metal, § 115, is examined according to (142). 146

β. The precipitate is not completely dissolved, a black residue being left; this indicates the presence of cobalt and nickel. Filter, wash the undissolved precipitate, and test the filtrate as directed (144); proceed with the residuary precipitate as follows:— 147

aa. Test a portion of it with borax, first in the outer, then in the inner blowpipe flame. If the bead in the oxidizing flame is violet whilst hot, and of a pale reddish-brown when cold, and turns in the reducing flame gray and turbid, nickel is present; but if the color of the bead is and remains blue, in both flames, and whether hot or cold, COBALT is present. As in the latter case the presence of nickel cannot be distinctly recognized; examine. 148

bb. The remainder of the precipitate by incinerating it together with the filter in a small porcelain capsule or crucible, heating the ash with some hydrochloric acid, filtering the solution, then evaporating nearly to dryness, and adding nitrate of potassa, and then acetic acid (§ 112, 10). The for- 149

mation of a yellow precipitate after standing in a warm place for some time confirms the presence of COBALT. Let the fluid, with the precipitate in it, stand for about 12 hours, then filter, and test the filtrate with solution of soda for NICKEL.

2. DETECTION OF THE BASES OF GROUPS III. AND IV. IN CASES WHERE PHOSPHATES, BORATES, OXALATES, OR SILICATES OF THE ALKALINE EARTHS, OR FLUORIDES OF THE METALS OF THE ALKALINE EARTHS, OR HYDRATED SILICA, MAY POSSIBLY HAVE BEEN THROWN DOWN ALONG WITH THESE BASES, *i.e.*, in cases where the original solution was acid or alkaline and a precipitate was produced by ammonia in the preliminary examination. See (**134**). **150**

Mix the fluid mentioned in the beginning of this paragraph (**134**) with some chloride of ammonium, then with ammonia just to alkaline reaction, lastly with sulphide of ammonium, until the fluid, after being shaken, smells distinctly of this reagent; shake the mixture until the precipitate begins to separate in flocks, warm gently for a time and filter.

Keep the FILTRATE, which contains, or may contain, the bases of Group II. and I., for subsequent examination according to the directions of § 198. Wash the precipitate *thoroughly* with water to which a very little sulphide of ammonium has been added, and then proceed with it as follows. To give a clear notion of the obstacles to be overcome in this analytical process I must remind you that it is necessary to examine the precipitate for the following bodies: Iron, nickel, cobalt (these show their presence to a certain extent by the black or blackish coloration of the precipitate), manganese, zinc, sesquioxide of chromium (the latter generally reveals its presence by the color of the solution), alumina;—baryta, strontia, lime, magnesia, which latter substances may have fallen down in combination with phosphoric acid, boracic acid, oxalic acid, silicic acid, or in form of fluorides. Besides these bodies, free silicic acid may also be contained in the precipitate as hydrate.

As the original substance must, under all circumstances, be afterwards examined for all acids that might possibly be present, it is not indispensable to test for the above enumerated acids at this stage of the analytical process; still, as it is often interesting to know the presence of these acids at once, more especially in cases where a somewhat large proportion of some alkaline earth has been found in the precipitate produced by sulphide of ammonium, a method for the detection of the acids in question will be found appended by way of supplement to the method for the detection of the bases. **151**

Remove the precipitate from the filter as soon as it is completely washed [else it may partially oxidize and be lost], with a small spatula, or by rinsing it off with the washing-bottle, and pour over it cold dilute hydrochloric acid in moderate excess. **152**

a. A RESIDUE REMAINS. Filter, and treat the filtrate as directed in (**154**). The residue, if it is black, may contain sulphide of nickel, and sulphide of cobalt, and besides these, sulphur and silicic acid. Wash, and examine a sample of it in conjunction with phosphate of soda and ammonia before the blowpipe, in the outer flame. If a silica skeleton remains undissolved (§ 153, 8), this proves the presence of silicic acid. If the color of the bead is blue, COBALT is present; if reddish, turning yellow on cooling, NICKEL. Should the color leave you in doubt, incinerate the filter containing the remainder of the residue, and test for cobalt and nickel by means of nitrite of potassa, as directed (**149**). **153**

b. NO RESIDUE IS LEFT (except perhaps a little sulphur, which may separate): absence of nickel and cobalt, at least in any notable proportion. **154**

Boil the solution until the sulphuretted hydrogen is expelled, and then proceed as follows:

α. Mix a small portion of the solution with dilute sulphuric acid. If a precipitate forms, this may consist of sulphates of BARYTA and STRONTIA, possibly also of sulphate of lime. Filter, wash the precipitate and test it either by the flame, according to the latter part of § 102, or decompose it by boiling or fusion with carbonated alkali, wash the carbonates produced, dissolve them in hydrochloric acid, and test the solution as directed § 198. Mix the fluid which has not been precipitated by dilute sulphuric acid, or the fluid filtered from the precipitate produced, with 3 volumes of spirit of wine. If a precipitate forms, this consists of sulphate of LIME. Filter, dissolve in water, and add oxalate of ammonia to the solution, as a confirmatory proof of the presence of lime. **155**

β. Boil a somewhat larger sample with some nitric acid, and test a small portion of the fluid with sulphocyanide of potassium for IRON;* mix the remainder with sesquichloride of iron in sufficient quantity to **156**

* Whether the iron was present as sesquioxide or as protoxide, must be ascertained by testing the original solution in hydrochloric acid with ferrocyanide of potassium and sulphocyanide of potassium. [Compare § 114, 8, note.]

make a drop of the fluid give a yellowish precipitate* when mixed, on a watch-glass, with a drop of ammonia; concentrate the fluid now until there is only a small quantity left; add to this some water, then a few drops of solution of carbonate of soda, just sufficient to *nearly* neutralize the free acid, and lastly carbonate of baryta in slight excess; stir the mixture, and let it stand in the cold until the fluid above the precipitate has become colorless. Filter now the precipitate (*aa*) from the solution (*bb*), and wash.

aa. Boil the *precipitate* for some time with solution of soda, filter, and test the filtrate for ALUMINA,† by heating with chloride of ammonium in excess. The part of the precipitate insoluble in solution of soda is examined for CHROMIUM by fusion with carbonate and nitrate of soda (§ 105, 8). **157**

bb. Add to the solution hydrochloric acid to acid reaction, heat to boiling, add dilute sulphuric acid as long as a precipitate of sulphate of baryta forms, and filter. Supersaturate the filtrate with ammonia and add sulphide of ammonium.

$\alpha\alpha$. *No precipitate forms:* absence of manganese and zinc. Mix the solution with oxalate of ammonia. If a precipitate of oxalate of LIME (which may be distinguished from separated *sulphur* by its being readily soluble in dilute hydrochloric acid) forms, filter, and test the filtrate with phosphate of soda for MAGNESIA. **158**

$\beta\beta$. *A precipitate forms.* Filter, and proceed with the filtrate according to the directions of $\alpha\alpha$ (**158**). The precipitate may consist of sulphide of manganese and sulphide of zinc, and may contain traces also of sulphide of cobalt and sulphide of nickel. Wash it with water containing some sulphide of ammonium, and then treat it with acetic acid, which will dissolve the sulphide of MANGANESE if any is present, leaving the other sulphides **159**

* The addition of sesquichloride of iron is necessary, to effect the separation of phosphoric acid and silicic acid which may be present.

† If the solution contains silicic acid, the precipitate taken for alumina may contain also silicic acid. A simple trial with phosphate of soda and ammonia on a platinum wire, in the blowpipe flame, will show whether the precipitate really contains silicic acid. Should this be the case, ignite the remainder of the supposed alumina precipitate on the cover of a platinum crucible, add some acid sulphate of potassa, fuse the mixture, and treat the fused mass with water, which will dissolve the alumina, leaving the silicic acid undissolved; precipitate the alumina from the solution by ammonia.

undissolved. Filter, boil the filtrate with solution of soda, and test the precipitate, which may form, with carbonate of soda in the lower blowpipe flame for MANGANESE. Free the residuary part of the precipitate, which acetic acid has failed to dissolve, by washing, from the acetic acid solution still adhering to it, and then treat it with dilute hydrochloric acid, which will dissolve the *zinc*, if any is present. Filter, add some nitric acid to the filtrate, and concentrate the mixture considerably by boiling; then add to it solution of soda in excess, boil, filter, if necessary, and test the filtrate with sulphide of ammonium for ZINC. Should a precipitate insoluble in solution of soda remain in the last operation, or should the dilute hydrochloric acid have left a black residue, test this precipitate and residue for COBALT and NICKEL, if you have not already previously detected the presence of these bodies; compare (**148** and **149**).

γ. If you have found alkaline earths in *α* or *β*, and **160** wish to know the acids in combination with which they have passed into the precipitate produced by sulphide of ammonium, this may be ascertained by making the following experiments with the remainder of the hydrochloric acid solution:—

aa. A portion is evaporated in a small capsule or **161** watch-glass in the water-bath to complete dryness, the residue is treated with hydrochloric acid, and subsequently with water. If SILICIC ACID were present it remains undissolved. The solution is tested by PHOSPHORIC ACID by means of the nitric solution of molybdate of ammonia (§ 145, 10).

bb. Mix another portion with carbonate of soda *in excess*, boil for some time, filter, and test one-half of the filtrate for OXALIC ACID, by acidifying it with acetic acid, and adding solution of sulphate of lime; the other half for BORACIC ACID, by slightly acidifying it with hydrochloric acid and testing with turmeric paper (§ 147 and § 148).

cc. Precipitate the remainder with ammonia, fil- **162** ter, wash and dry the precipitate, and examine it for FLUORINE according to § 149, 5.

§ 198.

(Separation and Detection of the Oxides of Group II., which are precipitated by Carbonate of Ammonia in Presence of Chloride of Ammonium, viz., Baryta, Strontia, L[illegible])

TO A SMALL PORTION OF THE FLUID IN WHICH AMMONIA SULPHATE OF AMMONIUM HAVE FAILED TO PRODUCE A PRECIPITATE (I[illegible]), OR OF THE FLUID FILTERED FROM THE PRECIPITATE FORMED, ADD CHLORIDE OF AMMONIUM, IF THE SOLUTION CONTAINS NO AMMONIACAL SALT, THEN CARBONATE OF AMMONIA AND SOME CAUSTIC AMMONIA, AND HEAT FOR SOME TIME VERY GENTLY (not to boiling).

1. NO PRECIPITATE FORMS: absence of any notable quantity of baryta, strontia, and lime. Traces of these alkaline earths may, however, be present; to detect them, add to another portion of the fluid some sulphate of ammonia (prepared by supersaturating dilute sulphuric acid with ammonia): if the fluid becomes turbid, it contains traces of BARYTA; add to a third portion some oxalate of ammonia; if the fluid turns turbid—which reaction may perhaps require some time to manifest itself—traces of LIME are present. Treat the remainder of the fluid as directed § 199, after having previously removed the traces of lime and baryta which may have been found, by means of the reagents that have served to effect their detection. **163**

2. A PRECIPITATE IS FORMED. Presence of LIME, BARYTA, or STRONTIA. Treat the entire solution with ammonia and carbonate of ammonia as above directed. After gently heating, filter, test portions of the filtrate with sulphate and oxalate of ammonia, for traces of lime and baryta, which it may possibly still contain, remove such traces, should they be found, by means of the said reagents, and examine the fluid, thus perfectly freed from baryta, strontia, and lime, for magnesia according to the directions of § 199. Wash the precipitate produced by carbonate of ammonia, dissolve it in the *least possible* amount of dilute hydrochloric acid, and add to a small portion of the fluid some *solution of sulphate of lime* (not too little). **164**

a. No precipitate is formed, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of baryta and strontia; presence of LIME. To remove all doubt, mix another sample with oxalate of ammonia.

b. A precipitate is formed by solution of sulphate of lime.

α. It is formed immediately; this indicates BARYTA. **165**

Besides this, strontia and lime may also be present.

Evaporate the remainder of the hydrochloric acid solution of the precipitate produced by carbonate of ammonia to dryness, digest the residue with strong alcohol, decant the fluid from the undissolved chloride of barium, dilute with an equal volume of water, mix with a few drops of hydrofluosilicic acid—which throws down the small portion of baryta that had dissolved in form of chloride of barium—allow the mixture to stand for some time; filter, and treat the filtrate with dilute sulphuric acid. The formation of a precipitate indicates strontia or lime or both these substances. The precipitate is filtered off after some time, washed with weak alcohol [a mixture of 4 volumes of so-called alcohol of 95 per cent. with 5 volumes of water], and boiled with solution of carbonate of soda to convert the sulphates into carbonates. The carbonates are collected on a small filter and washed with water dissolved in hydrochloric acid, and the solution is evaporated to dryness. Dissolve the residue in a little water and test a portion of the fluid with a dilute solution of sulphate of potassa (§ 99, 3). If a precipitate forms immediately, or in the course of half an hour, the presence of STRONTIA is demonstrated. In that case, let the fluid with the precipitate in it stand at rest for some time, then filter, and add ammonia and oxalate of ammonia to the filtrate. The formation of a white precipitate indicates LIME. If sulphate of potassa has failed to produce a precipitate, the remainder of the solution of the residue left upon evaporation is tested at once with ammonia and oxalate of ammonia for lime.

β. It is formed only after some time. Absence of baryta, presence of STRONTIA. Mix the remainder of the hydrochloric acid solution with sulphate of potassa, let the mixture stand for some time, then filter, and test the filtrate with ammonia and oxalate of ammonia for LIME. 166

§ 199.

(*Examination for Magnesia.*)

TO A PORTION OF THE FLUID IN WHICH CARBONATE, SULPHATE, AND OXALATE OF AMMONIA HAVE FAILED TO PRODUCE A PRECIPITATE (**163**) OR OF THE FLUID FILTERED FROM THE PRECIPITATES FORMED (**164**), ADD AMMONIA, THEN SOME PHOSPHATE

OF SODA, AND, SHOULD A PRECIPITATE NOT AT ONCE FORM, RUB THE INNER SIDES OF THE VESSEL WITH A GLASS ROD, AND THEN LET THE MIXTURE STAND FOR SOME TIME.

1. NO PRECIPITATE IS FORMED: absence of magnesia. Evaporate another portion of the fluid to dryness, and ignite gently. *If a residue remains*, treat the remainder of the fluid the same as the sample, and examine the residue, which by the moderate ignition to which it has been subjected has been freed from ammonia, for potassa and soda, according to the directions of § 200.—*If no residue is left*, this is a proof of the absence of the fixed alkalies; pass on to § 201. **167**

2. A PRECIPITATE IS FORMED: presence of MAGNESIA. As testing for alkalies can proceed with certainty only after the removal of magnesia, evaporate the remainder of the fluid to dryness, and ignite until all ammoniacal salts are removed. Warm the residue with water, add baryta-water (prepared from crystals of hydrate of baryta), as long as a precipitate continues to form,* boil, filter, add to the filtrate a mixture of carbonate of ammonia with some caustic ammonia in slight excess, heat for some time gently, filter, evaporate the filtrate to dryness, adding some chloride of ammonium during the process (to convert into chlorides the caustic alkalies that may have formed), ignite the residue gently, then dissolve it in a little water, precipitate, if necessary, once more, with ammonia and carbonate of ammonia, evaporate again, and if a residue remains, ignite this gently, and finally examine it according to the directions of § 200. **168**

§ 200.

(*Examination for Potassa and Soda.*)

YOU HAVE NOW TO EXAMINE FOR POTASSA AND SODA THE GENTLY IGNITED RESIDUE, FREE FROM SALTS OF AMMONIA AND ALKALINE EARTHS, WHICH HAS BEEN OBTAINED IN (**167**), OR IN (**168**).

Dissolve it in a little water, filter, if necessary, evaporate until there is only a small quantity of fluid left, and transfer one half of this to a watch-glass, leaving the other half in the porcelain dish.

1. To the one-half in the porcelain dish add, after cooling, a few drops of solution of *bichloride of platinum*. If a yellow, crystalline precipitate forms immediately, or after some time, POTASSA is present. Should no precipitate form, evaporate to dryness at a gentle heat, and treat the residue with a very small quantity of water or, if chlorides alone are present, **169**

* [In absence of sulphuric acid, or after it has been thrown down by baryta water or chloride of barium, *milk of lime* may be advantageously used to separate magnesia.]

with a mixture of water and alcohol, when the presence of minute traces of potassa will be revealed by a small quantity of a heavy yellow powder being left undissolved, § 92, 3.

2. To the other half of the fluid (in the watch-glass) add 170 some *antimonate of potassa*. If this produces at once or after some time a crystalline precipitate, SODA is present. If the quantity of soda present is only very trifling, it often takes twelve hours before minute crystals of antimonate of soda will separate; the operator should therefore wait that time for the possible manifestation of the reaction, before deciding, from its non-appearance, that no soda is present. As regards the form of the crystals, consult § 93, 2.

[The alkalies may also be conveniently tested for by *J. L. Smith's* method (§ 95), but care must be taken not to operate in an atmosphere containing ammonia vapors.]

§ 201.

(*Examination for Ammonia.*)

THERE REMAINS STILL THE EXAMINATION FOR AMMONIA. 171 Triturate some of the body under examination, or, if a fluid, a portion of the latter, together with an excess of hydrate of lime, and, if necessary, a little water. If the escaping gas smells of ammonia, if it restores the blue color of reddened litmus paper, and forms white fumes with hydrochloric acid vapors, brought into contact with it by means of a glass rod, AMMONIA is present. The reaction is the most sensitive, if the trituration is made in a small beaker, and the latter covered with a glass plate with a slip of moistened turmeric or moist reddened litmus paper adhering to the under side.

Complex Compounds.

A. 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.*

I. *In the Absence of Organic Acids.*

§ 202.

Consider, in the first place, *which* are the acids that form with the bases found, compounds soluble in water, and let this guide you in the examination. To beginners the table given in Appendix IV. will prove of considerable assistance.

1. The ACIDS of ARSENIC, as well as CARBONIC ACID, HYDRO- 172 SULPHURIC ACID, CHROMIC ACID, and SILICIC ACID, have generally been detected already in the course of testing for the bases; compare (67) and (68).

2. Add to a portion of the solution ch[illegible] of barium, or

* Consult also the explanations in Section III.

if lead, silver, or suboxide of mercury are present, nitrate of baryta, and, should the reaction of the fluid be acid, add ammonia to neutral or slightly alkaline reaction.

a. NO PRECIPITATE IS FORMED: absence of sulphuric acid, phosphoric acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acids, as well as of notable quantities of boracic acid and hydrofluoric acid.* Pass on to (**175**). **173**

b. A PRECIPITATE IS FORMED. Dilute the fluid, and add hydrochloric acid; if the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present. **174**

3. Add nitrate of silver to a portion of the solution. If this fails to produce a precipitate, test the reaction, and add to the fluid, if it is acid, dilute ammonia, taking care to add the reagent so gently and cautiously that the two fluids do not intermix; if the reaction is alkaline, on the other hand, add with the same care some dilute nitric acid, instead of ammonia, and watch attentively, whether a precipitate or a cloud forms in the layer between the two fluids. **175**

a. NO PRECIPITATE IS FORMED IN THE LAYER BETWEEN THE TWO FLUIDS, NEITHER IMMEDIATELY NOR AFTER SOME TIME. Pass on to (**181**); there is neither chlorine, bromine, iodine, cyanogen,† ferro- nor ferricyanogen present, nor sulphur; nor phosphoric acid, arsenic acid, arsenious acid, chromic acid, silicic acid, oxalic acid; nor boracic acid, if the solution was not too dilute. **176**

b. A PRECIPITATE IS FORMED. Observe the color‡ of it, then add nitric acid, and shake the mixture. **177**

α. The precipitate redissolves completely: absence of chlorine, bromine, iodine, cyanogen, ferro- and ferricyanogen, and also of sulphur. Pass on to (**181**).

β. A residue is left: chlorine, bromine, iodine, cyanogen, ferro- or ferricyanogen may be present; and if the residue is black or blackish, HYDROSULPHURIC ACID or a soluble METALLIC SULPHIDE.—The presence of sulphur may, if necessary, be readily established beyond **178**

* If the solution contains an ammoniacal salt in somewhat considerable proportion, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of these acids, since the baryta salts of most of them (not the sulphate) are, in presence of ammoniacal salts, more or less soluble in water.

† That the cyanogen in cyanide of mercury is not indicated by nitrate of silver has been mentioned (**73**).

‡ Chloride, bromide, cyanide, and ferrocyanide of silver, and oxalate, silicate, and borate of silver are white; iodide of silver, tribasic phosphate, and arsenite of silver are yellow; arsenate of silver and ferricyanide of silver are brownish-red; chromate of silver is purple-red; sulphide of silver is black.

doubt, by mixing another portion of the solution with some solution of sulphate of copper.

aa. Test another portion of the fluid for IODINE, and subsequently for BROMINE, by the methods described in § 160.

bb. Test a small portion of the fluid with sesqui- 179
chloride of iron for FERROCYANOGEN; and, if the color of the silver precipitate leads you to suspect the presence of FERRICYANOGEN, test another portion for this latter substance with protosulphate of iron.—If the original solution has an alkaline reaction, some hydrochloric acid must be added before the addition of the sesquichloride or the protosulphate of iron.

cc. CYANOGEN, if present in form of a simple metallic cyanide soluble in water, may usually be readily recognised by the smell of hydrocyanic acid which the body under examination emits, and which is rendered more strongly perceptible by addition of a little dilute sulphuric acid.—If no ferrocyanogen is present, the presence of cyanogen may be ascertained by the method given in § 158, 6.

dd. Should bromine, iodine, cyanogen, ferrocyano- 180
gen, ferricyanogen, and sulphur not be present, the precipitate which nitric acid has failed to dissolve, consists of CHLORIDE of silver.

However, should the analytical process have revealed the presence of any of the other bodies, a special examination for chlorine may become necessary, viz., in cases where the *quantity* of the precipitate will not enable the operator to pronounce with positive certainty on the presence or absence of the latter element.* In such cases, which are of rare occurrence, however, the methods given in § 160 are resorted to.

4. Test another portion for NITRIC ACID, by means of protosul- 181
phate of iron and sulphuric acid (§ 162).

5. To ascertain whether CHLORIC ACID is present, pour a little concentrated sulphuric acid over a small sample of the solid body under examination: ensuing yellow coloration of the acid resolves the question in the affirmative (§ 163).

You have still to test for phosphoric acid, boracic acid,

* Supposing, for instance, the solution of nitrate of silver to have produced a copious precipitate insoluble in nitric acid, and the subsequent examination to have shown mere traces of iodine and bromine, the presence of chlorine may be held to be demonstrated without requiring additional proof.

silicic acid, oxalic acid, and chromic acid, as well as for hydrofluoric acid.

For the first five acids test only in cases where both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. Compare also foot note to (**173**).

6. Test for PHOSPHORIC ACID, by adding to a portion of the **182** fluid, ammonia in excess, then chloride of ammonium and sulphate of magnesia (§ 145, 7). Very minute quantities of phosphoric acid are detected most readily by means of molybdic acid (§ 145, 10).

7. To effect the detection of OXALIC ACID and HYDROFLUORIC ACID, add chloride of calcium to a portion of the solution, which, if acid, must be rendered slightly alkaline by addition of ammonia. If chloride of calcium produces a precipitate which is not redissolved by addition of acetic acid, one or both bodies are present. Examine therefore now a sample of the original substance for fluorine, according to the directions of § 149, 5, another sample for oxalic acid, by the method given in § 148, 7.

8. Acidulate a portion of the fluid slightly with hydrochlo- **183** ric acid, and then test for BORACIC ACID, by means of turmeric paper (§ 147, 6).

9. Should SILICIC ACID not have yet been found in the course of testing for the bases, acidulate a portion of the fluid with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid (§ 153, 3).

10. CHROMIC ACID is readily recognised by the yellow or red color of the solution, and by the purple-red color of the precipitate produced by nitrate of silver.—If there remains the least doubt on the point, test for chromic acid with acetate of lead and acetic acid (§ 141, 7).

Complex Compounds.

A. I[redacted]BSTANCES SOLUBLE IN WATER.

[redacted]DETECTION OF ACIDS.

II. *In presence of Organic Acids.*

§ 203.

1. The ex[redacted]on for *inorganic acids*, inclusive of oxalic **184** acid, is made in the manner described in § 202. As the tartrates and citrates of baryta and silver are insoluble in water, tartaric acid and citric acid can be present only in cases where both chloride of barium and nitrate of silver have produced precipitates in the neutral fluid; still, in drawing a conclusion, you must bear in mind that the said salts are slightly soluble in solutions of salts of ammonia.

Before testing for *organic acids* it is necessary to remove all those bases whose presence might disturb the reactions, viz., all those belonging to Groups III. IV. V. and VI. This is accomplished by the methods already described at the beginning of § 187, to which the operator is referred.

The examination for the organic acids is then conducted as follows:—

2. Make a portion of the fluid feebly alkaline by addition of ammonia, add some chloride of ammonium, then chloride of calcium, shake vigorously, and let the mixture stand at rest from ten to twenty minutes. **185**

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of tartaric acid,* pass on to (**186**).

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER SOME TIME. Filter, wash, and keep the filtrate for further examination according to the directions of (**186**).

Digest and shake the precipitate with solution of soda, without applying heat, then dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID may be assumed to be present. Filter hot, and subject the precipitate to the ammonia and nitrate of silver test described in § 166, 8.

3. Mix the fluid in which chloride of calcium has failed to produce a precipitate, or that which has been filtered from the precipitate—in which latter case some more chloride of calcium is to be added—with alcohol. **186**

a. NO PRECIPITATE IS FORMED. Absence of citric acid and malic acid. Pass on to (**190**). **187**

b. A PRECIPITATE IS FORMED. Filter and treat the filtrate as directed in (**190**). As regards the precipitate, treat this as follows:— **188**

After washing with some alcohol, dissolve on the filter in a little dilute hydrochloric acid, add ammonia to the filtrate to feebly alkaline reaction, and then boil for some time.

α. THE FILTRATE REMAINS CLEAR. Absence of citric acid. Probable presence of MALIC ACID. Add alcohol again to the fluid, and test the lime precipitate in the manner directed § 169, to make sure whether malic acid is really present or not.

β. A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. Filter boiling, and test the filtrate for malic acid in the same manner as in *α*. To **189**

[* Tartaric acid may be easily overlooked unless the solution is *concentrated*.]

remove all doubt as to whether the precipitate is citrate of lime or not, it is advisable to dissolve once more in some hydrochloric acid, to supersaturate again with ammonia, and to boil; if the precipitate really consisted of citrate of lime, it will now be thrown down again. (Compare § 167, 3).

4. Heat the filtrate of (188) (or the fluid in which addition of alcohol has failed to produce a precipitate) (187), to expel the alcohol, neutralize *exactly* with hydrochloric acid, and add sesquichloride of iron. If this fails to produce a light brown, flocculent precipitate, neither succinic nor benzoic acid is present. If a precipitate of the kind is formed, filter, digest, and heat the washed precipitate with ammonia in excess; filter, evaporate the filtrate nearly to dryness, and test a portion for SUCCINIC ACID with chloride of barium and alcohol (§ 171); the remainder for BENZOIC ACID with hydrochloric acid (§ 172). Benzoic acid may generally be readily detected also in the original substance, by pouring some dilute hydrochloric acid over a small portion of the latter, which will leave the benzoic acid undissolved; it is then filtered and heated on platinum foil (§ 172, 1). 190

5. Evaporate a portion of the solution to dryness—if acid, after previous saturation with soda—introduce the residue, or a portion of the original dry substance, into a small tube, pour some alcohol over it, add about an equal volume of concentrated sulphuric acid, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of ACETIC ACID. This odor is rendered more distinctly perceptible by shaking the cooling or cold mixture. 191

6. To effect the detection of FORMIC ACID, add to a portion of the solution nitrate of silver in not too small a proportion, then soda until the fluid is *exactly* neutralized, and boil. If formic acid is present, reduction of the silver to the metallic state ensues (§ 175, 4). The reaction with nitrate of suboxide of mercury may be had recourse to as a conclusive test (§ 175, 5).* 192

* In presence of chromic acid the reduction of oxide of silver and suboxide of mercury is not a positive proof of the presence of formic acid. In cases where the two acids are present, the following method must be resorted to:—Mix the original solution with some nitric acid, add oxide of lead in excess, shake the mixture, filter, add to the filtrate dilute sulphuric acid in excess, and distil. Test the distillate as directed § 176. In presence of tartaric acid also it is the safest way to distil the formic acid first, with addition of dilute sulphuric acid.

Complex Compounds.

A. 2. Substances insoluble in Water, but soluble in Hydrochloric Acid, Nitric Acid, or Nitrohydrochloric Acid.

Detection of the Acids.

I. *In the absence of Organic Acids.*

§ 204.

In the examination of these compounds attention must be directed to all acids, with the exception of chloric acid. Cyanogen compounds and silicates are not examined by this method. (Compare § 207 and § 208.)

1. Carbonic acid, sulphur (in form of metallic sulphides), **193** arsenious acid, arsenic acid, and chromic acid, if present, have been found already in the course of the examination for bases; nitric acid, if present, has been detected in the course of the preliminary examination, by the ignition of the powdered substance in a glass tube (**8**).

2. Mix a sample of the substance with 4 parts of pure car- **194** bonate of soda and potassa, and, should it contain a metallic sulphide, add some nitrate of soda; fuse the mixture in a platinum crucible if there are no reducible metals present, in a porcelain crucible if reducible metals are present; boil the fused mass with water, and add a little nitric acid, leaving the reaction of the fluid, however, still alkaline; heat again, filter, and proceed with the filtrate according to the directions of § 202, to effect the detection of all the acids which were combined with the bases.*

3. As the phosphates of the alkaline earths are only incom- **195** pletely decomposed by fusion in conjunction with carbonate of soda and potassa, it is always advisable in cases where alkaline earths are present, and phosphoric acid has not yet been detected, to dissolve a fresh sample of the body under examination in hydrochloric acid or nitric acid, and after removal of silicic acid (§ 153, 3) and of arsenic acid (§ 136, 3 or 4) to test the solution for phosphoric acid with molybdic acid.

4. If in the course of the examination for bases, alkaline earths have been found, it is also advisable to test a separate portion of the body under examination for fluorine, by the method described in § 149, 5.

5. That portion of the substance under examination which **196** is treated as directed in (**194**), can be tested for silicic acid

* If the body examined has been found to contain a metallic sulphide, a separate portion of it must be examined for sulphuric acid, by heating it with hydrochloric acid, filtering, adding water to the filtrate, and then testing the fluid with chloride of barium.

only in cases where the fusion has been effected in a platinum crucible: in cases where a porcelain crucible has been used, it is necessary to examine a separate portion of the body for silicic acid, by evaporating the hydrochloric or nitric acid solution (§ 153, 3).

6. Examine a separate sample of the body for OXALIC ACID as directed in (§ 148, 6 or 7).

Complex Compounds.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE ACIDS.

II. *In presence of Organic Acids.*

§ 205.

1. Conduct the examination for inorganic acids according to the directions of § 204. **197**

2. Test for ACETIC ACID as directed § 174, 7.

3. Dissolve a portion of the compound under examination in the least possible amount of hydrochloric acid, filter, if necessary, and test the undissolved residue which may be left, for BENZOIC ACID by application of heat; add to the filtrate solution of carbonate of soda in considerable excess, and, besides this, also a little solid carbonate of soda, boil the mixture for a few minutes, and then filter the fluid from the precipitate. In the filtrate you have now all the organic acids in solution, combined with soda. Acidify the filtrate with hydrochloric acid, heat, and proceed according to (**185**). **198**

Complex Compounds.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE BOTH IN WATER AND IN HYDROCHLORIC ACID, NITRIC ACID, OR NITROHYDROCHLORIC ACID.

DETECTION OF THE BASES, ACIDS, AND NON-METALLIC ELEMENTS.

§ 206.

To this class belong the following bodies and compounds. **199**

SULPHATE OF BARYTA, SULPHATE OF STRONTIA, and SULPHATE OF LIME.*

SULPHATE OF LEAD† and chloride of lead.‡

* Sulphate of lime passes partially into the solution effected by water, and often completely into that effected by acids.

† Sulphate of lead may pass completely into the solution effected by acids.

‡ Chloride of lead can here only be found if the precipitate insoluble in acids has not been thoroughly washed with hot water.

CHLORIDE OF SILVER, bromide of silver, iodide of silver, cyanide of silver,* ferro- and ferricyanide of silver.†

SILICIC ACID and many SILICATES.

Native alumina, or alumina which has passed through a process of intense ignition, and many aluminates.

Ignited sesquioxide of chromium and chrome-ironstone (a compound of sesquioxide of chromium and protoxide of iron).

Ignited, and native binoxide of tin (tin-stone).

Some metaphosphates and some arsenates.

FLUORIDE OF CALCIUM and a few other compounds of fluorine.

SULPHUR.

CARBON.

Of these compounds those printed in small capitals are more frequently met with. As the silicates perform a highly important part in mineral analysis, a special chapter (§ 208—211) is devoted to them.

The substance under examination which is insoluble in water and in acids is in the first place subjected to the preliminary experiments here described in *a*—*e*, if the quantity at your disposal is not absolutely too small to admit of this proceeding; in cases where the quantity is insufficient for the purpose, the operator must omit this preliminary examination, and at once pass on to (**205**) bearing in mind, however, that the body may contain *all* the aforesaid substances and compounds.

a. Examine closely and attentively the physical state and **200** condition of the substance, to ascertain whether you have to deal with a homogeneous mass or with a mass composed of dissimilar particles; whether the body is sandy or pulverulent, whether it has the same color throughout, or is made up of variously-colored particles, &c. The microscope, or even a simple magnifying glass, will be found very useful at this stage of the examination.

b. Heat a small sample in a glass tube sealed at one end. **201** If brown fumes arise, and SULPHUR sublimes, this is of course a proof of the presence of that substance.

c. If the substance is black, this indicates, in most cases, **202** the presence of carbon (wood-charcoal, pit-coal, bone-black, lamp-black, graphite, &c.). Heat a small sample on platinum

* Bromide, iodide, and cyanide of silver are decomposed by boiling with nitrohydrochloric acid, and converted into chloride of silver; they can accordingly be found here only in cases where the operator has to deal with a substance which—as nitrohydrochloric acid has failed to effect its solution—is examined directly by the method described in this paragraph (§ 206).

† With regard to the examination of these compounds, compare also § 207.

foil over the blowpipe flame; if the substance (which blackens the fingers) is consumed, this may be held to be a positive proof of the presence of CARBON in some shape or other. Graphite, which may be readily recognized by its property of communicating its blackish-gray color to the fingers, to paper, &c., requires the application of oxygen for its easy combustion.

d. Warm a small sample, together with a small lump of cyanide of potassium and some water, for some time, filter, and test the filtrate with sulphide of ammonium. The formation of a brownish-black precipitate shows that the substance under examination contains a compound of SILVER. **203**

e. If an undissolved residue has been left in *d*, wash this thoroughly with water, and, if white, sprinkle a few drops of sulphide of ammonium over it; if it turns black, salts of LEAD are present. If, however, the residue left in *d* is black, heat it with some acetate of ammonia, adding a few drops of acetic acid, filter, and test the filtrate for LEAD, by means of sulphuric acid and hydrosulphuric acid.* **204**

The results obtained by these preliminary experiments serve to guide the operator now in his further course of proceeding.

1, *a*. SALTS OF LEAD ARE NOT PRESENT. Pass on to (**206**). **205**

b. SALTS OF LEAD ARE PRESENT. Heat the substance repeatedly with a concentrated solution of acetate of ammonia, until the salt of lead is completely dissolved out. Test a portion of the filtrate for CHLORINE, another for SULPHURIC ACID, and the remainder for LEAD, by addition of sulphuric acid in excess, and by hydrosulphuric acid. If acetate of ammonia has left a residue, wash this, and treat it as directed in (**206**).

2, *a*. SALTS OF SILVER ARE NOT PRESENT. Pass on to (**207**). **206**

b. SALTS OF SILVER ARE PRESENT. Digest the substance free from lead, or which has been freed from that metal by acetate of ammonia, repeatedly with cyanide of potassium and water, at a gentle heat (in presence of sulphur, in the cold), until all the salt of silver is removed. If an undissolved *residue* is left, wash this, and then proceed with it according to the directions of (**207**). Of the *filtrate*, which contains cyanide of potassium, mix the larger portion with sulphide of ammonium, to precipitate the silver. Wash the precipitated sulphide of silver, then dissolve it in nitric acid, dilute the solution,

* The presence of lead in silicates, *e. g.* in glass containing lead, cannot be detected by this method.

and add hydrochloric acid, to ascertain whether the precipitate really consisted of sulphide of silver. Test another small portion of the filtrate for SULPHURIC ACID.*

3. *a.* SULPHUR IS NOT PRESENT. Pass on to (208). 207

b. SULPHUR IS PRESENT. Heat the substance free from silver and lead in a covered porcelain crucible until all the sulphur is expelled, and, if a residue is left, treat this according to the directions of (208).

4. Mix the substance free from silver, lead, and sulphur 208
with 2 parts of carbonate of soda, 2 parts of carbonate of potassa, and 1 part of nitrate of potassa,† heat the mixture in a platinum crucible until the mass is in a state of calm fusion, place the red hot crucible on a thick, cold iron plate, and let it cool. By this means you will generally succeed in removing the fused mass from the crucible in an unbroken lump. Soak the mass now in water, boil, filter, and wash the residue until chloride of barium no longer produces a precipitate in the washings. (Add only the first washings to the filtrate.)

a. The solution obtained contains the acids which 209
were present in the substance decomposed by fluxing. But it may, besides these acids, contain also such bases as are soluble in caustic alkalies. Proceed as follows:—

α. Test a small portion of the solution for SULPHURIC ACID.

β. Test another portion with molybdic acid for PHOSPHORIC ACID and ARSENIC ACID. If a yellow precipitate forms, remove the arsenic acid which may be present with hydrosulphuric acid, and then test once more for phosphoric acid.

γ. Test another portion for FLUORINE (§ 149, 7).

δ. If the solution is yellow, CHROMIC ACID is present. To remove all doubt on the point, acidify a portion of the solution with acetic acid, and test with acetate of lead.

ε. Acidify the remainder of the solution with hydro- 210
chloric acid, evaporate to dryness, and treat the residue

* As the carbonate of potassa contained in the cyanide of potassium may have produced a total or partial decomposition of any sulphates of the alkaline earths which happened to be present.

† Addition of nitrate of potassa is useful even in the case of white powders, as it counteracts the injurious action of silicate of lead, should any be present, upon the platinum crucible. In the case of black powders, the proportion of nitrate of potassa must be correspondingly increased, in order that carbon, if present, may be consumed as completely as possible, and that any chrome ironstone existing in the compound may be more thoroughly decomposed.

with hydrochloric acid and water. If a residue is left which refuses to dissolve even in boiling water, this consists of SILICIC ACID. Test the hydrochloric acid solution now in the usual way for those bases which, being soluble in caustic alkalies, may be present.

b. Dissolve the residue left in (**208**) in hydrochloric acid (effervescence indicates the presence of alkaline earths), and test the solution for the bases as directed in § 193. (If much silicic acid has been found in (**210**), it is advisable to evaporate the solution of the residue to dryness, and to treat the residuary mass with hydrochloric acid and water, in order that the silicic acid remaining may also be removed as completely as possible.) **211**

5. If you have found in 4 that the residue insoluble in acids contains a silicate, treat a separate portion of it according to the directions of (**228**), to ascertain whether or not this silicate contains alkalies. **212**

6. If a residue is still left undissolved upon treating the residue left in (**208**) with hydrochloric acid (**211**), this may consist either of silicic acid, which has separated, or of an undecomposed portion of sulphate of baryta; it may, however, also be fluoride of calcium, and if it is dark-colored, chrome-ironstone, as the last-named two compounds are only with difficulty decomposed by the method given in (**208**). I would therefore remind the student that fluoride of calcium may be readily decomposed by means of sulphuric acid; and, as regards the decomposition of chrome-ironstone, I can recommend the following method, first proposed by *Hart:* Project the fine powder into 8 times the quantity of fused borax, stir the mixture frequently, and keep the crucible for half-an-hour at a bright red heat. Add now to the fusing mass carbonate of soda so long as effervescence continues, and then finally add 3 times the weight of the chrome-ironstone of a mixture of equal parts of carbonate of soda and nitrate of potassa, whilst actively stirring the mixture with a platinum wire. Let the mass cool, and, when cold, boil it with water. **213**

7. If the residue insoluble in acids contained silver, you have still to ascertain whether that metal was present in the original substance as chloride, bromide, iodide, &c., of silver, or whether it has been converted into the form of chloride of silver by the treatment employed to effect the solution of the original substance. For that purpose, treat a portion of the original substance with boiling water until the soluble part is completely removed; then treat the residuary portion in **214**

the same way with dilute nitric acid, wash the undissolved residue with water, and test a small sample of it for silver according to the directions of (**203**). If silver is present, proceed to ascertain the salt-radical with which the metal is combined; this may easily be effected by boiling the remainder of the residue in the first place with rather dilute solution of soda, filtering, and testing the filtrate, after acidifying it, for ferro- and ferricyanogen. Digest the washed residue now with finely granulated zinc and water, with addition of some sulphuric acid, and filter after the lapse of ten minutes. You may now at once test the filtrate for chlorine, bromine, iodine, and cyanogen; or you may first throw down the zinc with carbonate of soda, in order to obtain the salt-radicals in combination with sodium.

SECTION II.

PRACTICAL COURSE

IN PARTICULAR CASES.

I. Special Method of effecting the Analysis of Cyanides, Ferrocyanides, etc., insoluble in Water, and also of insoluble mixed Substances containing such Compounds.*

§ 207.

The analysis of ferrocyanides, ferricyanides, &c., by the common method is often attended by the manifestation of such anomalous reactions as easily mislead the analyst. Moreover, acids often fail to effect their complete solution. For these reasons it is advisable to analyze them, and mixtures containing such compounds, by the following special method:— **215**

Treat the substance with water until the soluble parts are entirely removed, and boil the residue with strong solution of potassa or soda; after a few minutes' ebullition add some carbonate of soda, and boil again for some time; filter, should a residue remain, and wash the latter.

1. The *residue*, if any has been left, is now free from cyanogen, unless the substance under examination contains cyanide of silver, in which case the residue would **216**

* Before entering upon this course of analysis, study well the special remarks to the paragraph (§ 207) in the Third Section.

of course still contain cyanogen. Examine the residue now by the common method, beginning at (**35**).

2. The *solution* or *filtrate*, which, if combinations of **217** compound cyanogen radicals (ferrocyanogen, cobalticyanogen, &c.) were originally present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by the process of boiling with carbonate of soda, and lastly also, such oxides as are soluble in caustic alkalies.

Treat the solution as follows:—

a. Mix the alkaline fluid with a *little* solution of hydro- **218** sulphuric acid. The addition of solution of hydrosulphuric acid or the passage of the gas through the solution until the liquid smells of it (*i. e.* until all the alkali is converted into a sulphuretted sulphide—hydrosulphate) is to be avoided, else alumina, and even sulphides of metals of the sixth group might be thrown down.

α. No permanent precipitate is formed. Absence of zinc and lead. Pass on to (**219**).

β. A permanent precipitate is formed. Add to the fluid sulphide of sodium, drop by drop, just sufficient to throw down from the alkaline solution the metals of groups IV. and V., heat moderately, filter, wash the precipitate, and treat the filtrate as directed in (**219**). Dissolve the washed precipitate in nitric acid, whereby sulphide of mercury may remain undissolved, and examine the solution for copper, lead, zinc, and other metals of the fourth group, which may, in the same way as copper, have passed into the alkaline solution by the agency of organic matters.

b. Mix the alkaline fluid, which contains now also sul- **219** phide of an alkali metal (and may therefore contain the sulphides of the sixth group (as sulphur salts), as well as sulphide of mercury, which is soluble in sulphides of the fixed alkalies), with water and with dilute nitric acid to acid reaction, and, if necessary, add more hydrosulphuric acid until the liquid smells strongly of the gas.

α. No precipitate is formed. Absence of mercury and of the oxides of the sixth group. Pass on to (**220**).

β. A precipitate is formed. Filter, wash the precipitate, and then examine it for mercury, and the metals of the sixth group, according to the directions of § 194.

c. The fluid, acidified with nitric acid, and therefore **220** abundantly supplied with nitrates of alkalies, may still contain the metals which, in combination with cyanogen,

form compound radicals (iron, cobalt, manganese, chromium), and, besides these, also alumina. You have to test it also for cyanogen, respectively, ferrocyanogen, cobalticyanogen, &c., and for other acids. Divide it, therefore, into two portions, α and β. Examine α for the acids acording to the directions of § 202 or § 203. (Cobalticyanogen may be recognised as such by its giving with salts of nickel greenish, with salts of manganese and zinc white precipitates in which cobalt may be detected with borax before the blowpipe.)

Evaporate β to dryness, and heat the residue to fusion. Pour the fused mass upon a piece of porcelain, boil with water, filter, and examine the residue for IRON, MANGANESE, COBALT, and ALUMINA. Test a portion of the filtrate (if yellow) for CHROMIC ACID, the remainder for ALUMINA—which may have passed partially or completely into the solution, through the agency of the caustic alkalies formed, in the process of fusion, from the nitrates of the alkalies present.

II. Analysis of Silicates.

§ 208.

Whether the body to be analyzed is a silicate, or contains one, is ascertained by the preliminary examination with phosphate of soda and ammonia before the blowpipe; since, in the process of fusion, the metallic oxides dissolve, whilst the separated silicic acid floats about in the liquid bead as a transparent, swollen mass (§ 153, 8). 221

The analysis of the silicates differs, strictly speaking, from the common course only in so far as the preliminary treatment is concerned, which is required to effect the separation of the silicic acid from the bases, and to obtain the latter in solution.

The silicates and double silicates are divided into two distinct classes, which require respectively a different method of analysis; viz., (1) silicates easily decomposable by acids (hydrochloric acid, nitric acid, sulphuric acid) and (2) silicates which are not decomposed or decomposed with difficulty, by acids. Many rocks are mixtures of these two kinds of silicates.

To ascertain to which of these two classes a silicate belongs, reduce it to a very fine powder, and digest a portion with hydrochloric acid at a temperature near the boiling point. If this fails to decompose it, try another portion with tolerably concentrated sulphuric acid, and apply heat. If this also fails, after some time, to produce the desired effect,

the silicate belongs to the second class. Whether decomposition has been effected by the acid or not may generally be learned from external indications, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely-pulverulent hydrate of silicic acid takes the place of the original heavy powder which grated under the glass rod with which it was stirred.

To ascertain whether the decomposition is complete the separated hydrate of silicic acid, after filtering and washing, is treated with boiling solution of carbonate of soda.

If complete solution takes place it shows that the silicate was wholly decomposed. If after repeated treatment a residue remains, it indicates that the silicate (or mixture of silicates) is but partially decomposed.

These preliminary tests decide whether the substance shall be further examined according to § 209 or § 210 or § 211.

Before proceeding further, test a portion of the pulverized compound also for *water*, by heating it in a perfectly dry glass tube. If the substance contains hygroscopic moisture it must first be dried by protracted exposure to a temperature of 212° F. Apply a gentle heat at first, but ultimately an intense heat, by means of the blowpipe; you may also conveniently combine with this a preliminary examination for *fluorine* (§ 149, 8).

A. Silicates decomposable by Acids.

§ 209.

*a. Silicates decomposable by hydrochloric acid or by nitric acid.**

222 1. Digest the finely pulverized silicate with hydrochloric acid (or nitric acid) at a temperature near the boiling point, until complete decomposition is effected, filter off a small portion of the fluid, evaporate the remainder, together with the silicic acid suspended therein, to dryness, and expose the residue to a temperature somewhat exceeding 212° F., with constant stirring, until no more, or very few, hydrochloric acid fumes escape; allow it to cool, moisten the residue with hydrochloric acid, or as the case may be, with nitric acid, afterwards add a little water, and heat gently for some time.

This operation effects the separation of the silicic acid, and the solution of the bases in the form of chlorides (or nitrates). Filter, wash the residue thoroughly, and examine the solu-

* Nitric acid is preferable to hydrochloric acid in cases where compounds of silver or lead are present.

tion by the common method, beginning at § 192, II. or III.* To be quite safe, the residuary silicic acid may be digested with ammonia, filtered, and the filtrate tested for silver, by supersaturation with nitric acid.

2. As in silicates, and more particularly in those decomposed by hydrochloric acid, there are often found other acids, as well as metalloids, the following observations and instructions must be attended to, that none of these substances may be overlooked:— 223

α. SULPHIDES of METALS and CARBONATES are detected in the process of treating with hydrochloric acid.

β. If the separated silicic acid is black, and turns subsequently white upon ignition in the air, this indicates the presence of CARBON or of ORGANIC SUBSTANCES. In presence of the latter, the silicates emit an empyreumatic odor upon being heated in a glass tube.

γ. Test the portion of the hydrochloric acid solution filtered off before evaporating (222), for SULPHURIC ACID, PHOSPHORIC ACID, and ARSENIC ACID: for sulphuric acid with chloride of barium, in a sample diluted with water: for arsenic acid by passing a stream of hydrosulphuric acid gas into the solution heated to 160° Fah., and further examination of the precipitate: for phosphoric acid by means of molybdic acid. The filtrate from the sulphide of arsenic, in case arsenic acid was present, will serve, after expulsion of excess of hydrosulphuric acid, to test for phosphoric acid.

* Minute traces of *titanic acid* are occasionally met with in silicates. The titanic acid present mostly passes into the hydrochloric acid solution, if the separation of the silicic acid has been effected on the water-bath, while a small portion separates with the silica. The titanic acid is detected in the following manner:

a. The silica is heated in a platinum dish with a mixture of hydrofluoric acid and sulphuric acid, and this is repeated until all the silica is dissipated as fluoride of silicon. Finally the residue is evaporated to dryness.

b. The solution that has been filtered from silica is precipitated with ammonia, the precipitate (which contains alumina, oxide of iron, &c., together with the rest of the titanic acid) is washed, dried, and ignited. It is now added to the residue obtained in *a*, the whole is fused with enough bisulphate of potassa to bring it into solution, and the heat is kept up until the greater part of the excess of sulphuric acid is driven off. After cooling the fused mass is dissolved in cold water (whereby a perfectly clear solution is obtained if the process has been successfully carried out, and all silica was removed). The solution is filtered if needful and largely diluted with water. Hydrosulphuric acid gas is now transmitted through the liquid until all sesquioxide of iron is reduced to protoxide. The liquid is now (without removal of the suspended sulphur) maintained for half an hour at a boiling heat, while a stream of carbonic acid gas is passed through it without interruption. The titanic acid is in this way gradually thrown down while all the bases remain in solution (*Th. Scheerer*).

c. The precipitate is collected on a filter, washed, ignited, and the residue is examined according to § 107, 10

δ. BORACIC ACID is best detected by fusing a portion of the substance in a platinum spoon with carbonate of soda, boiling the fused mass with water, and examining the solution for boracic acid by the method given in § 147, 6. 224

ε. With many silicates, boiling with water is sufficient to dissolve the metallic CHLORIDES present, which may then be readily detected in the filtrate by means of solution of nitrate of silver; the safest way, however, is to dissolve the mineral in dilute nitric acid, and test the solution with nitrate of silver.

ζ. Metallic FLUORIDES, which often occur in silicates in greater or smaller proportion, are detected by the method described § 149, 6.

b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.

Heat the finely pulverized mineral with a mixture of 3 parts of concentrated pure sulphuric acid, and 1 part of water (best in a platinum dish), finally drive off nearly all the sulphuric acid, boil the residue with hydrochloric acid, dilute, filter, and treat the filtrate as directed § 193; and the residue, which, besides the separated silicic acid, may contain also sulphates of the alkaline earths, &c., according to the directions of § 206. If you wish to examine silicates of this class for acids and salt-radicals, treat a separate portion of the substance according to the directions of § 210. 225

B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.*

§ 210.

As the silicates of this class are most conveniently decomposed by fusion with carbonate of soda and potassa, the portion so treated cannot, of course, be examined for alkalies. The analytical process is therefore properly divided into two principal parts, viz., a portion of the mineral is examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter.—Besides these, there are some other experiments required, to obtain information as to the presence or absence of other acids. 226

1. *Detection of the silicic acid and the bases, with the exception of the alkalies.*

* Silicates which are unaffected by boiling acids are with few exceptions decomposed when heated with a mixture of 3 parts concentrated sulphuric acid and 1 part of water, as well as by hydrochloric acid, to a temperature of 390° to 410° Fah. The silicate must be finely pulverized, and the heating is conducted in a sealed tube of Bohemian glass. (*Al. Mitscherlich.*)

Reduce the mineral to a very fine powder, mix this with 4 227
parts of carbonate of soda and potassa, and heat the mixture in a platinum crucible over a gas or *Berzelius* spirit-lamp, until the mass is in a state of calm fusion. Put the red-hot crucible on a thick, cold iron plate, and let it cool there; this will generally enable you to remove the fused cake from the crucible, in which case break the mass to pieces, and keep a portion for subsequent examination for acids. Put the remainder, or, if the mass still adheres to the crucible, the latter, with its contents, into a porcelain dish, pour water over it, add hydrochloric acid, and heat gently until the mass is dissolved, with the exception of the silicic acid, which separates in flocks. Remove the crucible from the dish, if necessary, evaporate the contents of the latter to dryness, and treat the residue as directed (222).

2. *Detection of the alkalies.*

To effect this, the silicates under examination must be 228
decomposed by means of a substance free from alkalies. Hydrofluoric acid or a metallic fluoride answers this purpose best; but fusion with hydrate of baryta will also accomplish the end in view.

a. DECOMPOSITION BY MEANS OF A METALLIC FLUORIDE.—Mix 1 part of the very finely pulverized mineral with 5 parts of fluoride of barium, or pure, finely pulverized fluoride of calcium, stir the mixture in a platinum crucible with concentrated sulphuric acid to a thickish paste, and heat gently for some time in a place affording a free escape to the vapors; finally heat a little more strongly, until the excess of sulphuric acid is completely expelled. Boil the residue now with water, add chloride of barium cautiously as long as a precipitate continues to form, then baryta-water to alkaline reaction, boil, filter, mix with carbonate of ammonia and some ammonia as long as a precipitate forms, and proceed exactly as directed (168).

b. DECOMPOSITION BY MEANS OF HYDRATE OF BARYTA. 229
Mix 1 part of the very finely pulverized substance with 4 parts of hydrate of baryta, expose the mixture for half an hour in a platinum crucible to the strongest possible heat of a good *Berzelius* or gas-lamp, and treat the fused or agglutinated mass with hydrochloric acid and water until it is dissolved; precipitate the solution with ammonia and carbonate of ammonia, filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, ignite, and test the residue for potassa and

soda as directed § 200. If the residue still contains magnesia, this may be readily removed, by adding to the aqueous solution of the residue a little pure oxalic acid, evaporating to dryness, igniting the dry mass, and then treating it with water, which will dissolve the alkalies as chlorides, and leave the magnesia undissolved. Filter, acidulate the filtrate with hydrochloric acid, evaporate to dryness, and examine the residue for potassa and soda.

[*c.* DECOMPOSITION BY MEANS OF CARBONATE OF LIME AND CHLORIDE OF AMMONIUM. Mix 1 part of the pulverized substance with 6 parts of precipitated carbonate of lime, and ¾ part of pulverized chloride of ammonium, place in a platinum crucible and treat to bright redness for 30 to 40 minutes. The crucible with its contents (which should be in a coherent, sintered, but not thoroughly fused condition), is placed in a beaker, covered with water and heated to near the boiling point for half an hour. The whole is then brought upon a filter, the filtrate, containing the alkalies, chloride of calcium and caustic lime, is treated with a little ammonia and with carbonate of ammonia in slight excess, and heated to boiling, filtered, and the filtrate evaporated to dryness and gently ignited to expel salts of ammonia. The residue is dissolved in a little water, one or two drops of carbonate of ammonia, and a drop of oxalate of ammonia added, the mixture is heated, filtered, the filtrate is evaporated to dryness, ignited, and the residual alkaline chlorides examined according to § 200. (*J. L. Smith*).] 229*

3. *Examination for fluorine, chlorine, boracic acid, phosphoric acid, arsenic acid, and sulphuric acid.*

Use for this purpose the portion of the fused mass reserved in (**227**), or, if necessary, fuse a separate portion of the finely pulverized substance with 4 parts of pure carbonate of soda and potassa until the mass flows calmly; boil the fused mass with water, filter the solution, which contains all the fluorine as fluoride of sodium, all the chlorine as chloride of sodium, all the boracic acid as borate, all the sulphuric acid as sulphate, all the arsenic acid as arsenate, and at least part of the phosphoric acid as phosphate of soda, and treat the filtrate as follows:— 230

a. Acidify a portion of it with nitric acid, and test for CHLORINE with nitrate of silver.

b. Test another portion for BORACIC ACID as directed § 147, 6.

c. Examine a third portion according to §149, 7 for FLUORINE.

d. The remainder is acidified with hydrochloric acid, and a small portion is tested with chloride of barium for SULPHURIC ACID; the rest of the solution is heated to 158° Fah., and tested for ARSENIC ACID by hydrosulphuric acid. If no precipitate is formed, the liquid—or if a precipitate separates, the filtrate from it—is evaporated to dryness, the residue is treated with hydrochloric acid and water, and the solution thus obtained is examined for PHOSPHORIC ACID by means of sulphate of magnesia, or a nitric solution of molybdate of ammonia (§ 145).

C. SILICATES WHICH ARE PARTIALLY DECOMPOSED BY ACIDS.

§ 211.

Most native rocks are mixtures of several silicates, of which the one is often decomposed by acids, the other not. If such mixtures were analyzed by the same method as the absolutely insoluble silicates, the analyst would indeed detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the rock. **231**

It is, therefore, advisable to examine separately those parts which show a different deportment with acids. For this purpose digest the very finely pulverized substance for some time with hydrochloric acid* at a very gentle heat, then filter off a small portion, evaporate the remainder to dryness, and expose to a temperature somewhat exceeding 212° F., with stirring, until no more, or very little hydrochloric acid vapor is evolved; let the residue cool, moisten it when cold with hydrochloric acid, heat gently with water, and filter.

The filtrate contains the bases of the decomposed part of the mixed mineral; examine this as directed (**222**). Test the portion first filtered off according to (**223**) γ, and portions of the original substance for other acids according to (**224**). The residue contains, besides the silicic acid separated from the bases by the action of the hydrochloric acid, that part of the mixed mineral which has resisted the action of the acid. Boil this residue with an excess of solution of carbonate of soda,† filter hot, and wash, first with hot solution of carbonate of soda, finally with boiling water. Treat the residuary undecomposed part of the mineral, from which the admixed free

* [Evolution of hydrogen gas may be due, in certain trap rocks, to presence of finely-divided metallic iron.]

† [According to A. Müller, caustic soda must be employed instead of carbonate of soda for taking up silica.]

silicic acid has thus been removed, according to the instructions given in § 210. In cases where it is of no consequence or interest to effect the separation of the silicic acid of the part decomposed by acids, you may omit the laborious treatment with carbonate of soda, and may proceed at once to the decomposition of the residue.

III. Analysis of Natural Waters.

§ 212.

In the examination of natural waters the analytical process 232
is simplified by the circumstance that we know from experience the elements and compounds which are usually found in them. Now, although a quantitative analysis alone can properly inform us as to the true nature and character of a water, since the differences between the various waters are principally caused by the different proportions in which the several constituents are respectively present, a qualitative analysis may yet render very good service, especially if the analyst notes with proper care, whether a reagent produces a faint or distinctly marked turbidity, a slight or copious precipitate, since these circumstances will enable him to make an approximate estimation of the relative proportions in which the several constituents are present.

I separate here the analysis of the common fresh waters (spring-water, well-water, brook-water, river-water, &c.) from that of the mineral waters, in which we may also include sea-water; for, although no well-defined limit can be drawn between the two classes, still the analytical examination of the former is necessarily far more simple than that of the latter, as the number of substances to be looked for is much more limited than in the case of mineral waters.

A. Analysis of Fresh Waters (Spring-water, Well-water, Brook-water, River-water, &c.).

§ 213.

We know from experience that the substances to be had 233
regard to in the analysis of such waters are the following:—

a. Bases: Potassa, soda, ammonia, lime, magnesia, protoxide of iron.

b. Acids, &c.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, nitrous acid, chlorine.

c. Organic Matters.

d. Mechanically suspended substances: Clay, &c.

The fresh waters contain indeed also other constituents besides those enumerated here, as may be inferred from the

origin and formation of springs, &c., and as has, moreover, been fully established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they escape detection, unless hundreds of pounds of the water are subjected to the analytical process. I omit, therefore, here the mode of their detection, and refer to § 214.

1. Boil one to two litres of the carefully collected water in 234
a glass flask or retort to one-half. This generally produces a precipitate. Pass the fluid through a perfectly clean filter (free from iron and lime), wash the precipitate well, after having removed the filtrate, and then examine both as follows:—

a. Examination of the precipitate.

The precipitate contains those constituents of the water 235
which were only kept in solution through the agency of free carbonic acid, or, as the case may be, in the form of bicarbonates, viz., carbonate of lime, carbonate of magnesia, hydrated sesquioxide of iron (which was in solution as bicarbonate of protoxide of iron, and precipitates upon boiling as sesquioxide, and if phosphoric acid is present, also in combination with that acid), phosphate of lime; and besides, silicic acid, and sometimes also sulphate of lime, if that substance is present in large proportion; and clay which was mechanically suspended in the water.

Dissolve the precipitate on the filter in the least possible quantity of dilute hydrochloric acid (effervescence indicates the presence of CARBONIC ACID), and mix separate portions of the solution:—

α. With sulphocyanide of potassium: red coloration indicates the presence of IRON. $KCNS$

β. After previous boiling, with ammonia: filter, if 236
necessary, mix the filtrate with oxalate of ammonia, and let the mixture stand for some time in a warm place. The formation of a white precipitate indicates the presence of LIME—in the form of carbonate, or also in that of sulphate if sulphuric acid is detected in γ. Filter, mix the filtrate again with ammonia, add some

* *Chatin* ("Journ. de Pharm. et de Chim.," 3 Sér. t. xxvii. p. 418) found iodine in all fresh-water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, &c., contains traces, even though extremely minute, of metallic iodides. According to *Marchand* ("Compt. Rend.," t. xxxi. p. 495), all natural waters contain iodine, bromine, and lithia. Van Ankum has demonstrated the presence of iodine in almost all the potable waters of Holland. And it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontia, fluorine, &c.

phosphate of soda, stir with a glass rod, and let the mixture stand for twelve hours. The formation of a white, crystalline precipitate, which is often visible only on the sides of the vessel when the fluid is poured out, indicates the presence of MAGNESIA (carbonate of);

γ. With chloride of barium, and let the mixture stand for twelve hours in a warm place. The formation of a precipitate—which, when very inconsiderable, is best seen if the supernatant clear fluid is cautiously decanted, and the small quantity remaining shaken about in the glass—indicates the presence of SULPHURIC ACID.

δ. Evaporate another portion to dryness, treat the residue with hydrochloric acid and water, filter and test the filtrate for PHOSPHORIC ACID by means of molybdic acid or sesquichloride of iron and acetate of soda (§ 145). 237

b. Examination of the filtrate.

α. Mix a portion of the filtrate with a little hydrochloric acid and chloride of barium. The formation of a white precipitate, which makes its appearance at once or perhaps only after standing some time, indicates SULPHURIC ACID. 238

β. Mix another portion with nitric acid, and add nitrate of silver. A white precipitate or a white turbidity indicates the presence of CHLORINE.

γ. Test a portion of the filtrate after acidifying with hydrochloric acid, for PHOSPHORIC ACID as in (237).

δ. Evaporate another and larger portion of the filtrate until highly concentrated, and test the reaction of the fluid. If it is alkaline, and a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, a CARBONATE of an alkali is present. Should this be the case, evaporate the fluid to perfect dryness, boil the residue with spirit of wine, filter, evaporate the alcoholic solution to dryness, dissolve the residue in a little water, and test the solution for NITRIC ACID* as directed § 162, 7, 8 or 9.

ε. Mix the remainder of the filtrate with some chloride of ammonium, add ammonia and oxalate of ammonia, and let the mixture stand for a considerable time. The formation of a precipitate indicates the presence of LIME. Filter, and test,—

* In many cases this circuitous but safe process is unnecessary, nitric acid being readily detected directly in the highly concentrated water.

aa. A small portion with ammonia and phosphate of soda for MAGNESIA.

bb. Evaporate the remainder to dryness, heat the residue to redness, remove the magnesia, which may be present (168) and test for POTASSA and SODA, according to the directions of § 200.

2. Acidify a tolerably large portion of the filtered water 239
with pure hydrochloric acid, and evaporate nearly to dryness; divide the residue into 2 parts, and—

a. Test the one part with hydrate of lime for AMMONIA (compare § 94, 3).

b. Evaporate the other part to dryness, moisten with hydrochloric acid, add water, warm, and filter, if a residue remains. The residue may consist of SILICIC ACID, and of CLAY which has been mechanically suspended in the water; these two substances may be separated from each other by boiling with solution of carbonate of soda. The precipitate is often dark-colored from the presence of organic substances; but it becomes perfectly white upon ignition.

3. Mix another portion of the water, fresh taken from the 240
well, &c., with lime-water. If a precipitate is thereby produced, FREE CARBONIC ACID OR BICARBONATES are present. If the former (free carbonic acid) is present, no permanent precipitate is obtained when a larger portion of the water is mixed with only a small amount of lime-water, since in that case soluble bicarbonate of lime is formed.

4. A portion is examined for NITROUS ACID* by mixing with 241
iodide of potassium-starch-paste (1 part of pure KI. 20 parts starch and 500 parts of *pure* water) and pure dilute sulphuric acid, and observing whether a blue coloration is produced at once or in a few minutes (§ 161, 1).

5. To detect the presence of ORGANIC MATTERS, evaporate a 242
portion of the water to dryness, and gently ignite the residue: blackening of the mass denotes the presence of organic substances. If this experiment is to give conclusive results, the evaporation of the water, as well as the ignition of the residue, must be conducted in a glass flask or a retort.

6. To detect putrefying organic matters or other substances recognisable by the odor, a flask is filled two-thirds full of the water, closed with the palm of the hand, and vigorously shaken; the smell is then noted. If hydrosulphuric acid is perceived proceed according to § 215, 3. To examine for organic odors in presence of hydrosulphuric

* Found by Schönbein in all rain and snow-waters.

acid combine the latter with help of a little sulphate of copper and test the odor again.

7. If you wish to examine the MATTERS MECHANICALLY SUSPENDED in a water (in muddy brook or river-water, for instance), fill a large glass bottle with the water, cork securely, and let it stand at rest for several days, until the suspended matter has subsided; remove now the clear supernatant fluid with the aid of a syphon, filter the remainder, and examine the sediment remaining on the filter. As this sediment may consist of the finest dust of various minerals, treat it first with hydrochloric acid, and examine the part insoluble in that menstruum in the manner directed § 208. 243

8. In order not to overlook oxide of lead, which sometimes exists in waters which are served through leaden pipes, a considerable quantity of the water is treated with hydrosulphuric acid gas left at rest for some time, and a black precipitate, should one be formed, is examined according to §196. For detecting extremely minute traces of lead 6 to 8 litres of water are acidulated with acetic acid and evaporated almost to dryness with addition of some acetate of ammonia to prevent the precipitation of sulphate of lead. The residue is filtered and precipitated with hydrosulphuric acid.

B. ANALYSIS OF MINERAL WATERS.

§ 214.

The analysis of mineral waters embraces a larger number of constituents than that of fresh water. The following are the principal of the additional elements to be looked for:— 244

CAESIA RUBIDIA, LITHIA, BARYTA, STRONTIA, ALUMINA, PROTOXIDE OF MANGANESE, BORACIC ACID, BROMINE, IODINE, FLUORINE, HYDROSULPHURIC ACID (*Hyposulphurous Acid*),* CRENIC ACID, and APOCRENIC ACID (*Formic Acid, Propionic Acid, &c., Nitrogen, Oxygen, Marsh Gas*).

The analyst has, moreover, to examine the muddy ochreous or hard sinter-deposits of the spring for ARSENIOUS ACID, ARSENIC ACID, OXIDE OF ANTIMONY, OXIDE OF COPPER, OXIDE OF LEAD, OXIDE OF COBALT, OXIDE OF NICKEL, and the oxides of other heavy metals. The greatest care is required in this examination, to ascertain whether these oxides come really from the water, and do not proceed from metal pipes, stopcocks, &c.† The absolute purity of the reagents employed

* With regard to the substances enclosed in parentheses consult my treatise on Quantitative Analysis, § 206, *et seq.*

† Compare "Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau," von Professor Dr. *Fresenius*; I. Der Kochbrunnen zu Wiesbaden; II. Die Mineralquellen zu Ems; III. die Quellen zu Schlangenbad; IV. die Quellen

in these delicate investigations must also be ascertained with the greatest care.

1. Examination of the Water.

a. Operations at the Spring.

§ 215.

1. Filter the water at the spring, if not perfectly clear, 245
through Swedish filter paper, and collect the filtrate in large bottles with glass stoppers. The sediment remaining on the filter, which contains, besides the flocculent matter suspended in the water, also those constituents which separate at once upon coming in contact with the air (hydrate of sesquioxide of iron, and compounds of sesquioxide of iron with phosphoric acid, silicic acid, arsenic acid), is taken to the laboratory, to be examined afterwards according to the directions of § 217.

2. The presence of free carbonic acid is usually suffi- 246
ciently visible to the eye. However, to convince yourself by positive reactions, test the water with fresh-prepared solution of litmus, and with lime-water. If carbonic acid is present, the former acquires a wine-red color; the latter produces turbidity, which must disappear again upon addition of the mineral water in excess.

3. Free hydrosulphuric acid is detected with the greatest 247
delicacy by the smell. For this purpose half fill a bottle with the mineral water, close with the hand, shake, remove the hand, and smell the bottle. In this way distinct traces of hydrosulphuric acid are often found, which would escape detection by reagents. However, if you wish to produce visible reactions, fill a large white bottle with the water, add a few drops of solution of acetate of lead in solution of soda, place the bottle on a white surface, and look in at the top, to see whether the water acquires a brownish color or deposits a blackish precipitate;—or half fill a large bottle with the water, and close with a cork to which is attached a small slip of paper, previously steeped in solution of acetate of lead and then moistened with a little solution of carbonate of ammonia; shake the bottle gently from time to time, and observe whether the paper slip acquires a brownish tint in the course of a few hours. If the addition of the solution of acetate of lead to the water has imparted a brown color to the fluid or produced a precipitate in it, whilst the reaction with the

zu Langenschwalbach; die Schwefelquelle zu Weilbach; die Mineralquelle zu Geilnau; VII. die neue Natronquelle zu Weilbach; published at Wiesbaden, by *Kriedel* und *Niedner*. 1850–1860.

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paper slip gives no result, this indicates that the water contains an alkaline sulphide, but no free hydrosulphuric acid.

4. Mix a wineglass-full of the water with some tannic acid, **248** another wineglass-full with some gallic acid. If the former imparts a blue violet, the latter a red violet color to the water, PROTOXIDE OF IRON is present. Instead of the two acids, you may employ infusion of galls, which contains them both. The coloration ensues only after some time, and increases from above where the air has access, downwards.

b. Operations in the Laboratory.

§ 216.

As it is always desirable to obtain even in the qualitative examination some information as to the quantitative composition of a mineral water, *i. e.* as to the proportions in which the several constituents are contained in it, it is advisable to analyze a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the relative proportions in which these constituents exist, and thus to determine the character of the water; and then to examine a large sample for substances that exist in smaller proportion, and finally a very large amount of the water or of sinter, for those elements which are present only in minute quantities. For this purpose proceed as follows:—

1. EXAMINATION FOR THOSE CONSTITUENTS OF THE WATER **249** WHICH ARE PRESENT IN LARGER QUANTITIES.

a. Boil about 3lbs. of the clear water, or of the filtrate, brought from the spring, in a glass flask for 1 hour, taking care, however, to add from time to time some distilled water, that the quantity of liquid may remain undiminished, and thus the separation of any but *those* salts be prevented which owe their solution to the presence and agency of carbonic acid. Filter after an hour's ebullition, and examine the precipitate and the filtrate as directed § 213.

b. Test for AMMONIA, SILICA, ORGANIC MATTERS, &c., as described § 213.

2. EXAMINATION FOR THOSE FIXED CONSTITUENTS OF THE **250** WATER WHICH ARE PRESENT IN MINUTE QUANTITIES ONLY.—Evaporate a large quantity (at least 20 lbs.) of the water in a silver or porcelain dish to dryness; conduct this operation with the most scrupulous cleanliness in a place as free as possible from dust. If the water contains no carbonate of an alkali, add pure carbonate of potassa to slight predominance. The process of evaporation may be conducted in the

first place over a gas-lamp, but ultimately the sand-bath must be employed. Heat the dry mass to very faint redness; if in a silver dish, you may at once proceed to ignite it; but if you have it in a porcelain dish, first transfer it to a silver or platinum vessel before proceeding to ignition. If the mass turns black in this process, ORGANIC MATTERS may be assumed to be present.*

Mix the residue thoroughly, that it may have the same composition throughout, and then divide it into 3 portions, one (*c*) amounting to about one-half, and each of the other two (*a* and *b*) to one-fourth.

a. EXAMINATION FOR IRON, AND PHOSPHORIC ACID.

Warm the portion *a* with some water, add perfectly **251** pure hydrochloric acid in moderate excess, digest for some time at a temperature near the boiling point, filter through paper washed with hydrochloric acid and water, and test.

α. A sample for IRON, by means of sulphocyanide of potassium.

β. The remainder is examined for PHOSPHORIC ACID with nitric solution of molybdate of ammonia (§ 145, 10).

b. EXAMINATION FOR FLUORINE.

Heat the portion *b* with water, add chloride of calcium **252** as long as a precipitate continues to form, let deposit; filter the fluid from the precipitate, which consists chiefly of carbonate of lime and carbonate of magnesia. After having washed and dried the precipitate, ignite, then pour water over it in a small dish, add acetic acid in slight excess, evaporate on the water-bath to dryness, heat until all smell of acetic acid has disappeared, add water, heat again, filter the solution of the acetates of the alkaline earths, wash, dry or ignite the residue, and test it for FLUORINE as directed § 149, 5.

c. EXAMINATION FOR THE REMAINING CONSTITUENTS **253** PRESENT IN MINUTE QUANTITIES.

Boil the portion *c* repeatedly with water, filter, and wash the undissolved residue with boiling water. You have now a residue (α), and a solution (β).

α. The *residue* consists chiefly of carbonate of lime,

* This inference is, however, correct only if the water has been effectually protected from dust during the process of evaporation; if this has not been the case, and you yet wish to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If you find organic matter, and wish to know whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed § 217, 3.

carbonate of magnesia, silica, and—in the case of chalybeate springs—hydrate of sesquioxide of iron. But it may contain also minute quantities of BARYTA, STRONTIA, ALUMINA, and PROTOXIDE OF MANGANESE, and must accordingly be examined for these substances.

Put the residue in a platinum or porcelain dish, pour water over it, add hydrochloric acid to slightly acid reaction, then 4 or 5 drops of dilute sulphuric acid, evaporate to dryness, moisten with hydrochloric acid, then add water, warm gently, filter, and wash the residue which is left undissolved.

aa. EXAMINATION OF THE RESIDUE INSOLUBLE IN HYDROCHLORIC ACID FOR BARYTA AND STRONTIA. 254

This residue will generally consist of silicic acid; but it may contain also sulphates of the alkaline earths and carbon. If there is much silicic acid present, remove this in the first place, as far as practicable, by boiling with dilute solution of soda; filter, wash the residue, if any has been left, dry, incinerate the filter in a platinum crucible, add some carbonate of soda and potassa, and, in presence of carbon, some nitrate of potassa, and ignite for some time. If the residue contains but little silicic acid, the treatment with solution of soda may be omitted, and the fusion with carbonate of potassa and soda, &c., at once proceeded with. Boil the fused mass with water, filter, wash thoroughly, dissolve the residue (which must have been left, if sulphates of the alkaline earths were present) on the filter in the least possible quantity of dilute hydrochloric acid, add an equal volume of spirit of wine, then some pure hydrofluosilicic acid, and let the mixture stand 12 hours. If in the course or at the end of the 12 hours a precipitate makes its appearance, this denotes the presence of BARYTA. Filter, and warm the filtrate in a platinum dish, adding from time to time some water, until the spirit of wine is quite driven off. Mix the fluid now with saturated solution of sulphate of lime. If this produces a precipitate, whether after some time or after several hours' standing, this precipitate consists of sulphate of STRONTIA. To make quite sure, examine it before the blowpipe (see § 99, 7).

The examination for baryta and strontia may be much more easily accomplished by help of the spec-

troscope. For this purpose, ignite what remains of the residue (free from silica), strongly over a blast lamp, wash the ignited mass with a little water, evaporate the clear liquid with hydrochloric acid to dryness and test the residue as directed § 102.

bb. EXAMINATION OF THE HYDROCHLORIC ACID SOLUTION FOR PROTOXIDE OF MANGANESE AND ALUMINA. **255**

Mix the solution in a flask with some pure chloride of ammonium, add ammonia until the fluid is just turning alkaline, then some yellow sulphide of ammonium, close the flask, which should be filled very nearly full, and let it stand for 24 hours in a moderately warm place. If a precipitate has formed at the end of that time, filter, dissolve the precipitate in hydrochloric acid, boil, add solution of potassa (§ 32, *c*) in excess, boil again, filter and test the filtrate for ALUMINA with chloride of ammonium;* the residue with carbonate of soda before the blowpipe for MANGANESE.

β. The *alkaline solution* contains the salts of the alkalies, and usually also magnesia and traces of lime. You have to examine it now for NITRIC ACID,† BORACIC ACID, IODINE, BROMINE, and LITHIA. Evaporate the fluid until *highly* concentrated, let it cool, and place the dish in a slanting position, that the small quantity of liquid may separate from the saline mass; pour a few drops of the concentrated solution in a watch-glass, acidify very slightly with hydrochloric acid, and test with turmeric paper for BORACIC ACID. Pour back into the dish the remainder of the liquid, of which you have just tested a few drops, evaporate, with stirring, to perfect dryness, and divide the residuary powder into 2 portions, one (*aa*) of two-thirds, the other (*bb*) of one-third. **256**

aa. EXAMINE THE LARGER PORTION FOR NITRIC ACID, IODINE, AND BROMINE. **257**

Put the powder into a flask, pour pure spirit of

* You are not justified in regarding this substance as an ingredient of the water, except in cases where the process of evaporation has been conducted in a platinum or silver dish, but not in a porcelain dish.

† The nitric acid originally present may have been destroyed by the ignition of the residue in (**250**), if the latter contained organic matter. If you have reason to fear that such has been the case, and you have not already found nitric acid in (**249**), examine a larger portion of non-ignited residue for that acid, according to the directions of (**257**).

wine of 90 per cent. over it, boil on the water bath, and filter hot; repeat the same operation a second and a third time. Mix the alcoholic extract with a few drops of solution of potassa, distil the spirit of wine off to within a small quantity, and let cool. If minute crystals separate, these may consist of nitrate of potassa; pour off the fluid, wash the crystals with some spirit of wine, dissolve them in a very little water, and test the solution for nitric acid, by means of indigo, brucia, or iodide of potassium, starch-paste, and zinc (§ 162). Evaporate the alcoholic solution now to dryness. If you have not yet found nitric acid, dissolve a small portion of the residue in a very little water, and examine the solution for that acid. Treat the remainder of the residue or, if it has been unnecessary to search for nitric acid, the entire residue, three times with warm alcohol, filter, evaporate the filtrate to dryness with addition of a drop of potassa lye, dissolve the residue in a very little water, add some starch-paste, acidify slightly with sulphuric acid, and test for iodine by adding some nitrite of potassa in solution, or a drop of solution of hyponitric acid in sulphuric acid. After having carefully observed the reactions, test the same fluid for bromine with chloroform or bisulphide of carbon and chlorine water in the manner described in § 160.

bb. EXAMINE THE SMALLER PORTION FOR LITHIA.

Warm the smaller portion of the residue, which, **258** if lithia is present, must contain that alkali as carbonate or phosphate, with water, add hydrochloric acid to distinctly acid reaction, evaporate *nearly* to dryness, and then mix with pure spirit of wine of 90 per cent., which will separate the greater portion of the chloride of sodium, and give all the lithia in the alcoholic solution. Drive off the alcohol by evaporation, and test the residue for LITHIA by means of the spectroscope. (§ 96, 3.)

If no spectroscope be at hand dissolve the residue in water mixed with a few drops of hydrochloric acid, add a little sesquichloride of iron, then ammonia in *slight* excess, and a small quantity of oxalate of ammonia, and let the mixture stand for some time; then filter off the fluid, which is now entirely free from phosphoric acid and lime; evaporate the filtrate to dryness, and gently ignite the residue,

until the salts of ammonia are expelled; treat the residue with some chlorine water (to remove the iodine and bromine) and a few drops of hydrochloric acid, and evaporate to dryness; add a little water and (to remove the magnesia) some finely divided oxide of mercury, evaporate to dryness, and gently ignite the residue, until the chloride of mercury is completely driven off; treat the residue now with a mixture of absolute alcohol and anhydrous ether, filter the solution obtained, concentrate the filtrate by evaporation, and set fire to the alcohol. If it burns with a carmine flame, LITHIA is present. By way of confirmation, convert the lithia found into phosphate of LITHIA. (§ 96, 3.)

3. EXAMINATION FOR SUBSTANCES WHICH ARE PRESENT IN EXTREMELY MINUTE QUANTITIES. **259**

1. Evaporate 2 or 3 cwt. of the water in a large, perfectly clean iron kettle until the salts which are soluble in water begin to separate. In case the water contains no carbonate of soda, add previously to the evaporation enough of this salt to give the water an alkaline reaction. Filter after the evaporation, wash the residue without uniting the washings to the first filtrate and examine:—

a. The precipitate according to the course beginning at (**261**).

b. The solution is acidulated with hydrochloric acid, chloride of barium added until all sulphuric acid is just thrown down, filtered, evaporated to dryness, and the residue extracted with alcohol of 90 *per cent.* The alcoholic solution is tested according § 96, last paragraph, for CAESIA and RUBIDIA.

2. Test a sample of the original water for NITROUS ACID according to (**241**). Should hydrosulphuric acid be present it must be removed by very cautious addition of sulphate of silver (silver must on no account remain in the solution). **260**

2. EXAMINATION OF THE SINTER-DEPOSIT.

§ 217.

1. Free the ochreous or sinter-deposit from impurities, by picking, sifting, elutriation, &c., and from the soluble salts adhering to it, by washing with water; digest a large quantity (about 200 grammes) of the residue with water and hydrochloric acid (effervescence: CARBONIC ACID) until the **261**

soluble part is completely dissolved; dilute, cool, filter, and wash the residue.

a. Examination of the filtrate.

262 α. The larger share of the filtrate is heated nearly to boiling, and solution of pure hyposulphite of soda added until all the iron is reduced to the state of protochloride. Carbonic acid is now passed through the still heated liquid until all or nearly all sulphurous acid is expelled, then hydrosulphuric acid is transmitted through it. The solution being diluted if necessary, the liquid is let stand in a moderately warm place until the odor of hydrosulphuric acid becomes faint, and is then filtered and washed.

263 It is now advantageous to displace the water by alcohol and to digest the precipitate with bisulphide of carbon until the larger portion of the free sulphur is removed. It is now gently warmed with yellow sulphide of ammonium, filtered, washed with water containing sulphide of ammonium, and the filtrate and wash waters are evaporated to dryness in a small porcelain capsule. The residue is moistened with pure red fuming nitric acid, warmed until most of the acid is expelled, carbonate of soda is added in excess and then nitrate of soda, and the whole heated to fusion. The fused mass is treated with cold water, filtered, the residue washed with dilute alcohol, and the aqueous solution tested for ARSENIC ACID (**121**) and (**122**); the residue for ANTIMONY, TIN and COPPER, by dissolving it in dilute hydrochloric acid and treating one-half in a platinum vessel with zinc (**123**) and adding to the other half ferrocyanide of potassium.

264 If a residue has been left upon treating the precipitate produced by hydrosulphuric acid with sulphide of ammonium, boil it, together with the filter, with a very little dilute nitric acid, filter, wash, and examine the contents of the filter, at first by pouring hydrosulphuric acid over it, that you may not overlook the possible presence of sulphate of lead, and test for BARYTA and STRONTIA as directed (**254**).

Mix the filtrate (the nitric acid solution) with some pure sulphuric acid, evaporate on the water-bath to dryness, and treat the residue with water. If this leaves an undissolved residue, the latter consists of sulphate of LEAD. To make quite sure, filter, wash the residue, treat it with hydrosulphuric acid water, and observe whether that reagent imparts a black color to

it. Test the fluid filtered from the sulphate of lead which may have separated, *a* with ammonia, *b* with ferrocyanide of potassium, for COPPER.

Of the fluid filtered from the precipitate produced by hydrosulphuric acid, examine in the first place a portion, after having evaporated to dryness and treated the residue with hydrochloric acid and water, with nitric solution of molybdate of ammonia for PHOSPHORIC ACID; mix the remainder in a flask with chloride of ammonium, ammonia, and yellow sulphide of ammonium, close the flask, and let it stand in a moderately warm place until the fluid above the precipitate looks no longer greenish, but yellow; filter, and wash the precipitate with water to which some sulphide of ammonium has been added. Dissolve the washed precipitate in hydrochloric acid, and test for COBALT, NICKEL, IRON, MANGANESE, ZINC, ALUMINA and SILICA as directed (**152**) to (**160**). Examine now the fluid filtered from the precipitate produced by sulphide of ammonium, for LIME and MAGNESIA in the usual way. **265**

β. Mix a portion of the highly diluted hydrochloric acid solution with chloride of barium, and let the mixture stand 12 hours in a warm place. The formation of a white precipitate indicates the presence of SULPHURIC ACID.

b. Examination of the residue.

This consists usually of silicic acid, clay, and organic matters, but it may also contain sulphate of baryta and sulphate of strontia. Boil in the first place with solution of soda or potassa, to dissolve the SILICIC ACID; then fuse the residue with carbonate of soda and potassa, and a little nitrate of potassa. Boil the mass with water, wash the residue, and then dissolve it in some hydrochloric acid, separate any silica which may be present, add to the hydrochloric solution ammonia, filter the fluid from the ALUMINA, &c., which may precipitate, evaporate the filtrate to dryness, gently ignite the residue, redissolve it in very little water, with addition of a drop of hydrochloric acid, and test for BARYTA and STRONTIA as directed (**254**). **266**

2. As regards the examination for FLUORINE, the best way is to take for this purpose a separate portion of the ochreous or sinter-deposit. Ignite (which operation will also reveal the presence of organic matters), stir with water, add acetic acid to acid reaction, evaporate until the acetic acid is completely expelled, and proceed as described in (**252**). **267**

3. Boil the ochreous or sinter-deposit for a considerable time with concentrated solution of potassa or soda, and filter.

a. Acidify a portion of the filtrate with acetic acid, add ammonia, let the mixture stand 12 hours, and then filter the fluid from the precipitate of alumina and hydrated silicic acid, which usually forms; again add acetic acid to acid reaction, and then a solution of neutral acetate of copper. If a brownish precipitate is formed, this consists of APOCRENATE of copper. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color has changed to blue, and warm. If a bluish-green precipitate is produced, this consists of CRENATE of copper.

b. If you have detected arsenic, use the remainder of the alkaline fluid to ascertain whether the arsenic existed in the sinter as arsenious acid or as arsenic acid. Compare § 137, 9.

IV. Analysis of Soils.

§ 218.

Soils must necessarily contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant the constituent elements of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition of that soil, and may accordingly save us, to some extent, the trouble of a qualitative analysis.

Viewed in this light, it would appear quite superfluous to make a qualitative analysis of soils still capable of producing plants; for it is well known that the ashes of plants contain almost invariably the same constituents, and the differences between them are caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is had also—in so far as may be done by a simple estimation—to the quantities and proportions of the several constituent ingredients, and to the state and condition in which they are found to be present in the soil, an analysis of the kind, if combined with an examination of the physical properties of the soil, and a mechanical separation of its component parts,*

* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition, compare *Fr. Schulze's* paper, "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journal f. prakt. Chemie, Vol. 47, p. 241.

may give most useful results, enabling the analyst to judge sufficiently of the condition of the soil, to supersede the necessity of a *quantitative* analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances in a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which are the constituents that are soluble in water;* which those that require an acid for their solution (in nature principally carbonic acid); and, finally, which those that are neither soluble in water nor in acids, and are not, accordingly, in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting question to answer is, whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agencies; and also what are the products which they yield upon their disintegration.†

In the analysis of soils, the constituents soluble in water, those soluble in acids, and the insoluble constituents must be examined separately. The examination of the organic portion also demands a separate process.

The analysis is therefore properly divided into the following four parts:

1. *Preparation and Examination of the Aqueous Extract.*

§ 219.

About two pounds (1000 grammes) of the air-dried soil are 269
used for the preparation of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty; in following the usual course, viz., digesting or boiling the earth with water, and then filtering, the fine particles of clay are speedily found to impede the operation, by choking up the pores of the filter; they also almost invariably render the

* Since the discovery that the soil, like porous charcoal, possesses the power of removing dissolved matters from solutions, the formerly received notion that those matters which are soluble in water, or in water containing carbonic acid, are free to move in the soil has been necessarily modified. We must conclude that the water extract of a soil does not accurately represent what is present in the soil in a form accessible to plants. Certainly it cannot contain these substances in the proportion in which they exist in the soil, because the absorptive power of the soil is exerted more forcibly towards some substances than towards others. Although for these reasons the analysis of the aqueous solution of a soil can no longer be valued as formerly, yet it is often of interest to know what substances really are dissolved by water from an earth, and I have therefore retained this chapter.

† For more ample information on this subject I refer the reader to *Fresenius'* "Chemie für Landwirthe, Forstmänner und Cameralisten;" published at Brunswick, by *F. Vieweg & Son*, 1847, p. 485.

filtrate turbid, at least the portion which passes through first. I have found the following method the most practical.* Close the neck of several middle-sized funnels with small filters of coarse blotting paper, moisten the paper, press it close to the sides of the funnels, and then introduce the air-dried soil, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed; fill the funnels with the soil to the extent of about two-thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back on the filter. Let the operation proceed quietly. When the first quantity of the fluid has passed, pour on more and continue the lixiviation until the weight of the filtrate is two or three times as great as that of the soil employed. Unite the several filtrates and set aside a portion of the washed earth for further examination.

270 *a.* Concentrate two-thirds of the aqueous solution by cautiously evaporating in a porcelain dish, filter off a portion, and test its reaction; put aside a portion of the filtrate for the subsequent examination for organic matters, according to the directions of (**280**). Warm the remainder, and add nitric acid. Evolution of gas indicates the presence of an ALKALINE CARBONATE. Then test with nitrate of silver for CHLORINE. *b.* Transfer the remainder of the concentrated fluid, together with the precipitate which usually forms in the process of concentration, to a small porcelain, or, which is preferable, a small platinum dish, evaporate to dryness, and cautiously heat the brownish residue over the lamp until complete destruction of the organic matter is effected. In presence of NITRATES this operation is attended with deflagration, which is more or less violent according to the greater or smaller proportion in which these salts are present. *c.* Test a small portion of the gently ignited residue with carbonate of soda before the blowpipe for MANGANESE. *d.* Warm the remainder with water, add some hydrochloric acid (effervescence indicates the presence of CARBONIC ACID), evaporate to dryness, heat a little more strongly, to effect the complete separation of the silicic acid, moisten with hydrochloric acid, add water, warm, and filter. The washed residue generally contains some carbon, and also a little clay—if the aque-

* Recommended by *Fr. Schulze* "Anleitung zur Untersuchung der Ackererden auf ihre wichtigsten physikalischen Eigenschaften und Bestandtheile."—Journ. f. prakt. Chemie, vol. 47, p. 241.

ous extract was not perfectly clear—and lastly SILICIC ACID. To detect the latter, make a hole in the point of the filter, rinse the residue through, boil with solution of carbonate of soda, filter, saturate with hydrochloric acid, evaporate to dryness, and treat the residue with water, which will leave the silicic acid undissolved.

e. Test a small portion of the hydrochloric acid solution with chloride of barium for SULPHURIC ACID; another portion with nitric solution of molybdate of ammonia for PHOSPHORIC ACID; a third portion with sulphocyanide of potassium for SESQUIOXIDE OF IRON. Add to the remainder a few drops of sesquichloride of iron (to remove the phosphoric acid), then ammonia cautiously until the fluid is slightly alkaline, warm a little, filter, throw down the LIME from the filtrate by means of oxalate of ammonia, and proceed for the detection of MAGNESIA, POTASSA, and SODA, in the usual way, strictly according to the directions of § 199. 271

f. Alumina is not likely to be found in the aqueous extract. (*Fr. Schulze* never found any.) However, if you wish to test for it, boil the ammonia precipitate obtained in (271) with pure solution of soda or potassa, filter, and test the filtrate with chloride of ammonium. 272

g. If you have detected iron, test a portion of the remaining third of the aqueous extract with ferricyanide of potassium, another with sulphocyanide of potassium, both after previous addition of some hydrochloric acid: this will indicate the degree of oxidation in which the iron is present. Mix the remainder of the aqueous extract with a little sulphuric acid, evaporate on the water-bath nearly to dryness, and test the residue for AMMONIA, by adding hydrate of lime. 273

2. *Preparation and Examination of the Acid Extract.*

§ 220.

1. Heat about 50 grammes of the soil from which the part soluble in water has been removed as far as practicable,* with moderately strong hydrochloric acid (effervescence indicates CARBONIC ACID) for several hours on the water-bath, filter, and make the following experiments with the filtrate, which, owing to the presence of sesquichloride of iron, has in most cases a yellow color:— 274

Test a small portion of it with sulphocyanide of potassium 275

* Complete lixiviation is generally impracticable.

for SESQUIOXIDE OF IRON, another with ferrocyanide of potassium for PROTOXIDE OF IRON.

2. Test a small portion with chloride of barium for SULPHURIC ACID, another with molybdate of ammonia for PHOSPHORIC ACID.

3. Mix a larger portion of the filtrate with ammonia to neutralize the free acid, then with yellowish sulphide of ammonium; and let the mixture stand in a warm place until the fluid looks yellow; then filter, and test the filtrate in the usual way for LIME, MAGNESIA, POTASSA, AND SODA. **276**

4. Dissolve the precipitate obtained in 3, in hydrochloric acid, evaporate the solution to dryness, moisten the residue with hydrochloric acid, add water, warm, filter, and examine the filtrate according to the directions of (**150**), for IRON, MANGANESE, ALUMINA, and, if necessary, also for lime and magnesia, which may have been thrown down by the sulphide of ammonium, in combination with phosphoric acid. **277**

5. The separated SILICIC ACID obtained in 4 is usually colored by organic matter. It must, therefore, be ignited to obtain it pure.

6. If it is a matter of interest to ascertain whether the hydrochloric acid extract contains ARSENIC ACID, OXIDE OF COPPER, &c., treat the remainder of the solution first with hyposulphite of soda, then with hydrosulphuric acid, as directed in (**262**) to (**264**). **278**

7. Should you wish to look for FLUORINE, ignite a fresh portion of the earth, and then proceed according to the directions of (**230**).

3. *Examination of the Inorganic Constituents insoluble in Water and Acids.*

§ 221.

The operation of heating the lixiviated soil with hydrochloric acid (**274**) leaves still the greater portion of it undissolved. If you wish to subject this undissolved residue to a chemical examination, wash, dry, and sift, to separate the large and small stones from the clay and sand; moreover, separate the two latter from each other by elutriation. Subject the several portions to the analytical process given for the silicates (§ 208). **279**

4. *Examination of the Organic Constituents of the Soil.**

§ 222.

The organic constituents of the soil, which exercise so great an influence upon its fertility, both by their physical

* Compare *Fresenius'* "Chemie für Landwirthe, Forstmänner und Cameralisten;" published at Brunswick, by *F. Viewey and Son*, 1847, §§ 282—285.

and chemical action, are partly portions of plants in which the structure may still be recognised (fragments of straw, roots, seeds of weeds, &c.), partly products of vegetable decomposition, which are usually called by the general name of HUMUS, but differ in their constituent elements and properties, according to whether they result from the decay of the nitrogenous or non-nitrogenous parts of plants—whether alkalies or alkaline earths have or have not had a share in their formation—whether they are in the incipient or in a more advanced stage of decomposition. To separate these several component parts of humus would be an exceedingly difficult task, which, moreover, would hardly repay the trouble; the following operations are amply sufficient to answer all the purposes of a qualitative analysis of the organic constituents of a soil.

a. Examination of the Organic Substances soluble in Water.

Evaporate the portion of the filtrate of (**270**), which has been put aside for the purpose of examining the organic constituents, on the water-bath to perfect dryness, and treat the residue with water. The ulmic, humic, and geic acids, which were in the solution in combination with bases, remain undissolved, whilst crenic acid and apocrenic acid are dissolved in combination with ammonia; for the manner of detecting the latter acids, see (**268**). **280**

b. Treatment with an Alkaline Carbonate.

Dry a portion of the lixiviated soil, and sift to separate the fragments of straw, roots, &c., together with the small stones, from the finer parts; digest the latter for several hours, at a temperature of 176°—194° F., with solution of carbonate of soda, and filter. Mix the filtrate with hydrochloric acid to acid reaction. If brown flakes separate, these proceed from ulmic acid, humic acid, or geic acid. The larger the quantity of ulmic acid present the lighter, the larger that of humic acid or geic acid, the darker the brown color of the flakes. **281**

c. Treatment with Caustic Alkali.

Wash the soil boiled with solution of carbonate of soda (*b*) with water, boil several hours with solution of potassa, replacing the water in proportion as it evaporates, dilute, filter and wash. Treat the brown fluid as in *b*. The ulmic and humic acids which separate now, are new products resulting from the action of boiling solution of potassa upon the ulmine and humine originally present. **282**

V. Detection of Inorganic Substances in Presence of Organic Substances.

§ 223.

The impediments which the presence of coloring, slimy, and other organic substances throws in the way of the detection of inorganic bodies, and that the latter can often be effected only after the total destruction of the organic admixture, will be readily conceived, if we reflect that in dark-colored fluids changes of color or the formation of precipitates escape the eye, that slimy fluids cannot be filtered, &c. Now, as these difficulties are very often met with in the analysis of medicinal substances, and more especially in the detection of inorganic poisons in articles of food or in the contents of the stomach, and, lastly, also in the examination of plants and animals, or parts of them, for their inorganic constituents, I will here point out the processes best adapted to lead to the attainment of the object in view, both in the general way and in special cases.

1. *General Rules for the Detection of Inorganic Substances in Presence of Organic Matters, which by their Color, Consistence, &c., impede the Application of the Reagents, or obscure the Reactions produced.*

§ 224.

We confine ourselves here, of course, to the description of the most generally applicable methods, leaving the adaptation of the modifications which circumstances may require in special cases, to the discretion of the analyst.

1. The substance under examination dissolves in water, but the solution is dark colored or of slimy consistence. 283

a. Boil a portion of the solution with hydrochloric acid, and gradually add chlorate of potassa, until the mixture is decolorized and perfectly fluid; heat until it no longer exhales the odor of chlorine, then dilute with water, and filter. Examine the filtrate in the usual way, commencing with § 193. Compare also § 228.

b. Boil another portion of the solution for some time with nitric acid, filter, and test the filtrate for silver, potassa, and hydrochloric acid. If the nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, &c., this method is often altogether preferable to all others.

c. Alumina and sesquioxide of chromium might escape detection by this method, because ammonia and

sulphide of ammonium fail to precipitate these oxides from fluids containing non-volatile organic substances. Should you have reason to suspect the presence of these oxides, mix a third portion of the substance with carbonate of soda and chlorate of potassa, and project the mixture, in small portions at a time, into an ignited crucible. After cooling, the fused mass is treated with water, the solution is tested for chromic acid and alumina, and the residue for alumina as directed § 106. The alumina is now found by acidifying with nitric acid, and then adding ammonia; the chromium—as alkaline chromate—in the filtrate, by means of acetate of lead, after addition of acetic acid.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE FLUID ADMITS OF FILTRATION. **284**

Filter, and treat the filtrate either as directed § 192, or, should it require decolorization, according to the directions of (**283**). The residue may be of various kinds.

a. IT IS FATTY. Remove the fatty matters by means of ether, and should a residue be left, treat this as directed § 178.

b. IT IS RESINOUS. Use alcohol instead of ether, or apply both liquids successively.

c. IT IS OF A DIFFERENT NATURE, *e.g.*, woody fibre, &c.

α. Dry, and ignite a portion of the dried residue in a porcelain or platinum vessel, until total or partial incineration is effected; boil the residue with nitric acid and water, and examine the solution as directed (**109**); if a residue has been left, treat this according to the directions of § 206.

β. Examine another portion for the heavy metals and for acids in the manner directed in (**283**) and (**281**); since in *α*, besides the compounds of mercury which may be present, arsenic, cadmium, zinc, &c., may volatilize.

γ. Test the remainder for ammonia, by triturating it together with hydrate of lime.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART. **285**

Treat the substance in the same manner as the residue in (**284**). As regards the charred mass (**284**) c. *α*, it is often desirable to boil the mass, carbonized at a gentle heat, with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ash.

2. *Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, &c., in Chemico-legal Cases.**

§ 225.

The chemist is sometimes called upon to examine an article of food, the contents of the stomach of an individual, a dead body, &c., with a view to detect the presence of some poison, and thus to establish the fact of a wilful or accidental poisoning; but it is more frequently the case that the question put to him is of a less general nature, and that he is called upon to determine whether a certain substance placed before him contains a *metallic* poison; or, more pointedly still, whether it contains arsenic, or hydrocyanic acid, or some other particular poison—as it may be that the symptoms point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question. 286

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether *a certain poison*, *e.g.*, arsenic, is present or not, if he adopts a course of proceeding which will not only permit the detection of the *one* poison specially named, the presence of which may be suspected on insufficient grounds, but will moreover inform him as to the presence or absence of other similar poisons.

But we must not go too far in this direction either; if we were to attempt to devise a method that should embrace *all* poisons, we might unquestionably succeed in elaborating such a method at the writing-desk; but practical experience would but too speedily convince us that the intricate complexity inseparable from such a course, must necessarily impede the easy execution of the process, and impair the certainty of the results, to such an extent indeed, that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances permit usually at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, I give here,—

1. A method which ensures the detection of the minutest traces of arsenic, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

* Compare: *a Fresenius*, "die Stellung des Chemikers bei gerichtlich chemischen Untersuchungen," &c. Annal. der Chemie und Pharm. 49, 275); and *b. Fresenius* and *v. Babo's* "Abhandlung über ein neues, unter allen Umständen sicheres Verfahren zur Ausmittelung und quantitativen Bestimmung des Arsens bei Vergiftungsfällen." —Annal. der Chemie und Pharmacie, 49, 287.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for vegeto-alkalies.

3. A method to effect the detection of phosphorus, which does not interfere with the examination for other poisons.

This section does not, therefore, profess to supply a complete guide in every possible case or contingency of chemico-legal investigations. But the instructions given in it are the tried and proved results of my own practice and experience. Moreover, they will be found sufficient in most cases, the more so as I shall append to the Section on the vegeto-alkalies, the description of a process by which the detection of these latter poisons in criminal cases may be effected.

I. Method for the Detection of Arsenic (with due Regard to the possible Presence of other Metallic Poisons).

§ 226.

287 Of all metallic poisons arsenic is the most dangerous, and at the same time the one most frequently used, more particularly for the wilful poisoning of others. And again, among the compounds of arsenic, arsenious acid (white arsenic) occupies the first place, because—(1) It kills even in small doses; (2) It does not betray itself, or at least very slightly, by the taste; and (3) It is but too readily procurable.

As arsenious acid dissolves in water only sparingly and—on account of the difficulty with which moisture adheres to it—very slowly, the greater portion of the quantity swallowed exists usually in the body still in the undissolved state; as, moreover, the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—no matter what opinion may be entertained about the normal presence of arsenic in the bones, &c.—this much is certain, that at all events *arsenious acid in grains or powder* is never normally present in the body, the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious acid in substance—and this end may indeed usually be attained.

A. Method for the Detection of undissolved Arsenious Acid.

288 1. If you have to examine some article of food, substances rejected from the stomach, or some other matter of the kind, mix the whole as uniformly as may be practicable, reserve one-third for unforeseen contingencies, and mix the other

two-thirds in a porcelain dish with distilled water, with a stirring rod; let the mixture stand a little, and then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat this latter operation several times, if possible, with the same fluid, pouring it from the second dish back into the first, &c. Finally, wash once more with pure water, remove the fluid, as far as practicable, and try whether you can find in the dish small, white, hard grains which feel gritty and grate under the glass rod. If not, proceed as directed § 227 or § 228. But if so, put the grains, or part of them, on blotting-paper, removing them from the dish with the aid of pincers, when dry weigh them and try the deportment of one or several grains upon heating in a glass tube, and of some other grains upon ignition with a splinter of charcoal (compare § 135, 2, and 11). If you obtain in the former experiment a white crystalline sublimate, in the latter a lustrous arsenical mirror, the fact is clearly demonstrated that the grains selected and examined consisted really of arsenious acid. If you wish to determine the quantity of the poison, unite the contents of both dishes, and proceed as directed § 227, or § 228.

2. If a stomach is submitted to you for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and (*a*), search the inside coat for small, white, hard, sandy grains. The spots occupied by such grains are often reddened; they are also frequently found firmly imbedded in the membrane. (*b*) Mix the contents in the dish uniformly, put aside one-third for unforeseen contingencies, and treat the other two-thirds as in 1. The same course is pursued also with the intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious acid cannot be found in grains, if the poison has been introduced through the mouth. If you have found grains of the kind described, examine them as directed in 1; if not, proceed according to the instructions of § 227 or § 228.

B. Process for detecting Compounds of Arsenic and of other Metals, which are Soluble in Water, by means of Dialysis.

§ 227.

If in method *A.* no arsenious acid, in the solid state, has 289
been found and the operator proceeds directly to the process described in § 228, in which the organic matters are destroyed by chlorate of potassa and hydrochloric acid, he must remain ignorant of the condition in which any arsenic that may be found, exists, for the solution will contain arsenic acid no

matter what may have been the compound originally present. Any compound of arsenic or of other metals that is soluble in water, may, however, be detected by a dialytic* experiment.

For this purpose the *dialyser* shown in Fig. 34, may be employed. A hoop of wood, or gutta-percha, or of glass (cut from a broken jar), of 2 or more inches in depth, and 8 to 10

Fig. 34.

inches in diameter, has a wetted disk of parchment-paper (which should exceed the hoops in diameter by 3 or 4 inches), rather loosely secured to it by thread or a ring of elastic rubber. The parchment-paper must not be porous. Its soundness will be ascertained by sponging the upper surface with water, and then observing that no wet spots show themselves on the opposite side. Defects may be remedied by applying liquid albumin, and then coagulating the same by heat. When the dialyser is ready, the mass to be examined (residue and liquid of § 226, A), after the addition of two-thirds of the stomach, intestines, &c., cut into small pieces, if these are under investigation, and allowing the whole to digest for 24

* Dialysis, which is a late discovery of Graham's (Phil. Mag. (4) xxiii, and Ann. Ch. u. Ph. cxxi. 63), is founded on the different relation of substances in aqueous solution towards moist membranes. One class of bodies, the *crystalloids*, rapidly penetrate permeable membranes; the other class, the *colloids*, are comparatively destitute of this power. The first class comprises all crystallizable bodies. The second class includes the uncrystallizable substances, such as glue, gum, dextrin, caramel, tannin, albumin, so-called extractive matters, hydrated silica, &c. The membrane used for dialysis must consist of a colloidal substance, *e.g.*, bladder, or best of all, parchment paper. It is placed in contact with pure water on one side. The action, Graham explains by supposing that crystalloids attract and take up the water which exists in the moist colloid membrane, and thus acquire a medium for diffusion, whereas the colloids are incapable of separating water from the membrane, and therefore cannot penetrate it.

hours at a temperature of about 90° Fah., is brought into the dialyser so as not to fill it to more than the depth of ½ an inch, and the whole is then floated or supported on the surface of pure water, contained in a larger vessel, the amount of which should be about 4 times that of the liquid in the dialyser. When 24 hours have elapsed, one-half to three-fourths of the crystalloids that were placed in the dialyser have passed into the outer vessel whose contents usually appear colorless. This *diffusate* is now concentrated in the water bath, acidulated with hydrochloric acid, and finally treated with hydrosulphuric acid and further examined as directed (**291**). In case a soluble compound of arsenic or of any other metal was present, the corresponding sulphide is thus procured in a state of almost entire purity. By continuing the dialysis—placing under the dialyser fresh portions of water—all the crystalloid substances may be ultimately obtained in nearly a pure state. Afterwards, the residue may be examined for insoluble metallic compounds according to § 228.

*C. Method for the Detection of Arsenic in whatever Form of Combination it may exist, which allows also a Quantitative Determination of that Poison, and permits at the same time the Detection of other Metallic Poisons which may be present.**

§ 228.

If you have found no arsenious acid by the method described in *A*, nor any soluble compound of arsenic by dialysis, evaporate the mass in the porcelain dish, which has been diluted by washing with water (see *A*, 1), on the water-bath, to a pasty consistence. If you have to analyze a stomach, intestinal tube, &c., cut this into pieces, and add two-thirds to the mass in the dish, in case this has not been done already in the dialysis.

In examining other parts of the body (the lungs, liver, &c.), cut them also into pieces, and use two-thirds for the analysis. The process is divided as follows:†

* This method is essentially the same as that which I have elaborated and published in 1844, jointly with *L. v. Babo;* compare "Annal. der Chemie und Pharmacie," Bd. 49, p. 308. I have since that time had frequent occasion to apply it; I have also had it tried by others, under my own inspection, and *I have invariably found it to answer the purpose perfectly.*

† It is hardly needful to observe that in such extremely delicate experiments the vessels and reagents used in the process must be perfectly free from arsenic, from heavy metals in general, and indeed from every impurity.

1. *Decolorization and Solution.*

Add to the matters in the porcelain dish, whose quantity **290** e. g., may equal 4 to 8 ounces, an amount of pure hydrochloric acid about equal to, or somewhat exceeding the weight of the dry substances present, and sufficient water to give to the entire mass the consistence of a thin paste. In no case should the amount of hydrochloric acid exceed one-third that of the liquid employed. Heat the dish now on the water-bath, adding every five minutes about two grammes (half a drachm) of chlorate of potassa to the hot fluid, with stirring, and continue the same operation until the contents of the dish show a light-yellow color and a perfectly homogeneous appearance, and are quite fluid. The water which is lost by evaporation, should be renewed from time to time. When this point is attained, add again a portion of chlorate of potassa, and then remove the dish from the water-bath. When the contents are quite cold, transfer them cautiously to a linen strainer or to a white filter, according to the greater or less quantity of substance; allow the whole of the fluid to pass through, and put the filtrate aside. Wash the residue well with hot water, and dry it; then mark it I., and reserve for further examination, according to the instructions of (**303**). Evaporate the washings on the water-bath to about 3 or 4 oz. (about 100 grm.), add this, together with any precipitate that may have formed therein, to the principal filtrate, and then heat the whole in the water-bath, replacing the water that evaporates, until the odor of chlorine has entirely or nearly vanished.

2. *Treatment of the Solution with Hydrosulphuric Acid* **291** (Separation of the Arsenic as Tersulphide, and, respectively, of all the Metals of Groups V. and VI. in form of Sulphides.)

The fluid obtained in 1, which amounts to about three or four times the quantity of hydrochloric acid used, is brought into a flask, heated to about 158° Fah., and a slow stream of washed hydrosulphuric acid gas is transmitted through it for about 12 hours, and then, the gas being still passed into it, it is allowed to cool. Now rinse the delivery pipe with some ammonia, add the ammoniated solution thus obtained, after acidulating it, to the principal fluid, cover the beaker lightly with unsized paper, and put it in a moderately warm place (about 86° F.), until the odor of hydrosulphuric acid has nearly disappeared. Collect the precipitate obtained in this manner on a moderately sized filter, and wash, until the wash-

ings are quite free from chlorine. Concentrate the filtrate and washings somewhat, mix the fluid in a suitably sized flask with ammonia to alkaline reaction, then with sulphide of ammonium, closely cork the flask, which must now be nearly full, and reserve for further examination according to the instructions of (**307**).

3. *Purification of the Precipitate produced by Hydrosulphuric Acid.* **292**

Thoroughly dry the precipitate obtained in 2—which, besides organic matters and *free sulphur*, must contain, in form of tersulphide, the whole of the arsenic present in the analyzed substance, as well as, in form of sulphides, all the metals of Groups V. and VI. which may happen to be present—together with the filter, in a small porcelain dish, heated on the water-bath; add pure fuming nitric acid (perfectly free from chlorine), drop by drop, until the mass is completely moistened, and then evaporate on the water-bath to dryness. Moisten the residue uniformly all over with pure hydrated sulphuric acid, previously warmed; then heat for two or three hours on the water-bath, and finally on the air-sand- or oil-bath at a somewhat higher, though still moderate temperature (338° F.), until the charred mass becomes friable, and a small sample of it—to be returned afterwards to the mass—when mixed with water and then allowed to subside, gives a colorless fluid; should the fluid standing over the sediment show a brownish tint, or the residue, instead of being friable, consist of a brown, oily liquid, add to the mass some cuttings of pure Swedish filtering paper, and continue the application of heat. By attending to these rules you will always completely attain the object in view, viz., the destruction of the organic substances, without loss of any of the metals. Warm the residue on the water-bath, with a mixture of 8 parts of water and 1 part of hydrochloric acid, filter, wash the undissolved part thoroughly with hot, distilled water, with addition of a little hydrochloric acid, and add the washings, which must be concentrated if necessary, to the filtrate.

Dry the washed carbonaceous residue, then mark it II., and reserve for further examination according to the instructions given in (**304**).

4. Preliminary Examination for Arsenic and other Metallic Poisons of Groups V. and VI. (Second Precipitation with Hydrosulphuric Acid.) **293**

The clear fluid obtained in 3 contains all the arsenic which

may have been present, in form of arsenious acid, and may contain also tin, antimony, mercury, copper, bismuth, and cadmium. Supersaturate a small portion of it cautiously and gradually with a mixture of carbonate of ammonia and some ammonia, and observe whether a precipitate is thereby produced. Acidify the supersaturated sample of the fluid with hydrochloric acid, which will redissolve the precipitate that may have been produced by ammonia; then return the sample to the fluid, and treat the latter with hydrosulphuric acid in strict accordance with the directions of (**291**).

This process may lead to three different results, which are to be carefully distinguished.

a. The hydrosulphuric acid fails at first to produce a precipitate; but after the fluid has stood for some time, a trifling white or yellowish-white precipitate separates. In this case probably no metals of Groups V. and VI. are present. Nevertheless, treat the filtered and washed precipitate as directed in (**297**), to guard even against overlooking the minutest traces of arsenic, &c. **294**

b. A precipitate is formed, of a pure yellow color like that of tersulphide of arsenic. Take a small portion of the fluid, together with the precipitate suspended therein, add some ammonia, and shake the mixture for some time, without application of heat. If the precipitate dissolves readily and, with the exception of a trace of sulphur, completely, and if, in the preliminary examination (**293**), carbonate of ammonia has failed to produce a precipitate, arsenic alone is present, and no other metal (tin or antimony), at all events, no quantity worth noticing. Mix the solution of the small sample in ammonia with hydrochloric acid to acid reaction, return the acidulated sample to the fluid from which it was taken, and which contains the yellow precipitate produced by the hydrosulphuric acid, and proceed as directed in (**297**). If, on the other hand, the addition of ammonia to the sample completely or partially fails to redissolve the precipitate, or if, in the preliminary examination (**293**), carbonate of ammonia has produced a precipitate, there is reason to suppose that another metal is present, perhaps with arsenic. In this latter case also, add to the sample in the test-tube hydrochloric acid to acid reaction, return the acidulated sample to the fluid from which it was taken, which contains the yellow precipitate produced by the hydrosulphuric acid, and proceed as directed in (**298**). **295**

c. A precipitate is formed, which is not yellow. In **296**

that case you have to assume that other metals are present, perhaps with arsenic. Proceed as directed in (**298**).

5. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, in Cases where the Results of the Examination in* (**295**) *lead to the Assumption that Arsenic alone is present.* Determination of the Weight of the Arsenic. **297**

As soon as the fluid precipitated according to the directions of (**293**) has nearly lost the smell of sulphuretted hydrogen transfer the yellow precipitate to a small filter, wash thoroughly, pour upon the still moist precipitate solution of ammonia, and wash the filter—on which, in this case, nothing must remain undissolved, except sulphur—thoroughly with dilute ammonia; evaporate the ammoniacal fluid in a small, accurately tared porcelain dish, on the water-bath, dry the residue at 212° F. until its weight suffers no further diminution, and weigh. If it is found, upon reduction, that the residue consisted of perfectly pure tersulphide of arsenic, calculate for every part of it 0·8049 of arsenious acid, or 0·6098 of arsenic. Treat the residue in the dish according to the instructions given in (**300**).

6. *Treatment of the Yellow Precipitate produced by Hydrosulphuric Acid, in Cases where the Results of the Examination in* (**295**), *or in* (**296**), *lead to the Assumption that another Metal is present—perhaps with Arsenic.* Separation of the Metals from each other. Determination of the Weight of the Arsenic. **298**

If you have reason to suppose that the precipitate produced by hydrosulphuric acid (**293**) contains other metals, perhaps with arsenic, proceed as follows:—As soon as the precipitation is thoroughly accomplished, and the smell of sulphuretted hydrogen nearly disappeared, pour the precipitate on a small filter, wash thoroughly, perforate the point of the filter, and rinse the contents with the washing-bottle into a little flask, using the least possible quantity of water for the purpose; add to the fluid in which the precipitate is now suspended, first ammonia, then some yellowish sulphide of ammonium, and let the mixture digest for some time at a gentle heat. Should part of the precipitate remain undissolved, filter this off, wash, perforate the filter, rinse off the residuary precipitate, mark it III., and reserve for further examination according to the instructions given in (**305**). Evaporate the filtrate, together with the washings, in a small porcelain dish, to dryness. Treat the residue with some pure fuming nitric

acid (free from chlorine), nearly expel the acid by evaporation, and then add, as *C. Meyer* was the first to recommend, gradually, and in small portions at a time, a solution of pure carbonate of soda until it predominates. Add now a mixture of 1 part of carbonate and 2 parts of nitrate of soda, in sufficient, yet not excessive quantity, evaporate to dryness, and heat the residue very gradually to fusion. Let the fused mass cool, and, when cold, extract it with cold water. If a residue remains undissolved, filter, wash with a mixture of 299
equal parts of spirit of wine and water, mark it IV., and reserve for further examination, according to the direction of (306). Mix the solution, which must contain all the arsenic as arsenate of soda, with the washings, previously freed from alcohol by evaporation, add gradually and cautiously pure dilute sulphuric acid to strongly acid reaction, evaporate in a small porcelain dish, and when the fluid is tolerably concentrated, add again sulphuric acid, to see whether the quantity first added has been sufficient to expel all nitric and nitrous acids; heat now very cautiously until heavy fumes of hydrated sulphuric acid begin to escape; then let the liquid cool, dilute with water, bring into a small flask, and, while the liquid is kept at a temperature of 158° Fah., pass a slow current of washed hydrosulphuric acid gas into it for at least 6 hours, then, continuing the stream of gas, let it cool. If arsenic is present, a yellow precipitate will form. When the precipitate has completely subsided, and the fluid has nearly lost the smell of sulphuretted hydrogen, filter, wash the precipitate, dissolve it in ammonia, and proceed with the solution as directed in (297), to determine the weight of the arsenic.

7. *Reduction of the Sulphide of Arsenic.*

The production of metallic arsenic from the sulphide, which 300
may be regarded as the keystone of the whole process, demands the greatest care and attention. The method recommended in § 135, 12, viz., to fuse the arsenical compound, mixed with cyanide of potassium and carbonate of soda, in a slow stream of carbonic acid gas, is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with some other body, more particularly antimony; on which account it is more especially adapted for medico-legal investigations.

The reduction should be made with great care; the apparatus should be entirely filled with carbonic acid, and the stream of this gas should be made sufficiently slow before applying heat to the mixture. It is best to employ an apparatus which admits

of perfectly regulating the gaseous current. For the evolution flask § 135, 12 may be conveniently substituted the arrangement shown in Fig. 35, which is easily constructed from the ordinary stock of a laboratory. The stoppers are best made of vulcanized rubber [though corks soaked in melted tallow answer a good purpose]. The clamp by which the issue of gas is controlled should be adjustable by means of a screw [or wedge].

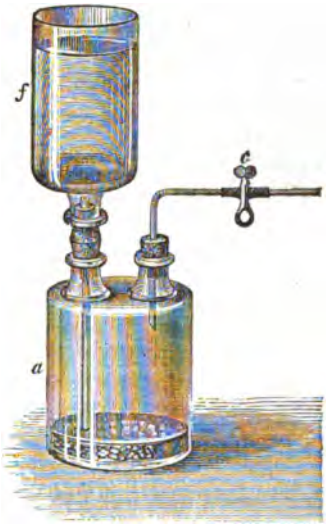

Fig. 35.

For the process of reduction, you may proceed at once with the sulphide of arsenic. Take care, if possible, not to use the whole of the residue in the dish, obtained by the evaporation of the ammoniacal solution, but only a portion of it, so that the process may be repeated several times, if necessary. Should the residue be too trifling to admit of being divided into several portions, dissolve it in a few drops of ammonia, add a little carbonate of soda, and evaporate on the water-bath to dryness, taking care to stir the mixture during the process; divide the dry mass into several portions, and proceed to reduction.

*Otto** recommends to convert the sulphide first into arsenic **301**
acid, and then to reduce the latter with cyanide of potassium. The following is the process given by him to effect the conversion of the sulphide into the acid; pour concentrated nitric acid over the sulphide of arsenic in the dish, evaporate, and repeat the same operation several times, if necessary, and then remove every trace of nitric acid by repeatedly moistening the residue with water, and drying again; when the nitric acid is *completely* expelled, treat the residue with a few drops of water, add carbonate of soda in powder, to form an alkaline mass, and thoroughly dry this in the dish, with frequent stirring, taking care to collect the mass within the least possible space in the middle of the dish. The dry mass thus obtained is admirably adapted for reduction. I can, from the results of my own experience, fully confirm this statement of *Otto;* but I must once more repeat, that it is

* "Anleitung zur Ausmittelung der Gifte," *von Dr. Fr. Jul. Otto*, p. 36.

indispensable for the success of the operation that the residue should be perfectly free from *every trace* of nitric acid or nitrate; otherwise deflagration is sure to take place during the process of fusion with cyanide of potassium, and, of course, the experiment will fail.

When the operation is finished, cut off the reduction tube **302** at *c* (see Fig. 30), set aside the fore part, which contains the arsenical mirror, put the other part of the tube into a cylinder, pour water over it, and let it stand some time; then filter

Fig. 36.

the solution obtained, add to the filtrate hydrochloric acid to acid reaction; then again some hydrosulphuric acid, and observe whether this produces a precipitate. In cases where the reduction of the sulphide of arsenic has been effected in the direct way, without previous conversion to arsenic acid, a trifling yellow precipitate will usually form; had traces of antimony been present, the precipitate would be orange-colored and insoluble in carbonate of ammonia. When all the soluble salts of the fused mass have been dissolved out, examine the metallic residue, which may be left behind, for traces of tin and antimony; these being the only metals that can possibly be present if the instructions here given have been strictly followed. Should *appreciable* traces of these metals, or of either of them, be found, proper deduction and correction must be made in calculating the weight of the arsenic.

8. *Examination of the reserved Residues, marked severally* I., II., III., *and* IV., *for other Metals of the Fifth and Sixth Groups.*

a. Residue I. Compare (**290**).

This may contain chloride of silver and sulphate of **303** lead, possibly also binoxide of tin. Incinerate the residue (I.) in a porcelain dish, burn the carbon with the aid of some nitrate of ammonia, extract the residue with water, dry the part left undissolved, and then fuse it with cyanide of potassium in a porcelain crucible. When the fused mass is cold, treat it with water until all that is soluble in it is completely removed; warm the residue with nitric acid, and proceed as directed in § 184.

b. Residue II. Compare (**292**).

The carbonaceous residue which is obtained by the **304**

purification of the crude sulphide by means of nitric acid and sulphuric acid, may more especially contain lead, mercury, and tin; antimony and bismuth may also be present.

Heat the residue for some time with nitrohydrochloric acid, and filter the solution; wash the undissolved residue with water mixed with some hydrochloric acid, add the washings to the filtrate, and treat the dilute fluid thus obtained with hydrochloric acid; should a precipitate form, examine this according to the instructions given in § 194. Incinerate the residue insoluble in nitrohydrochloric acid, fuse the ash in conjunction with cyanide of potassium, and proceed with the fused mass as directed in (**302**).

c. *Residue III.* Compare (**298**).

Examine the precipitate insoluble in sulphide of ammo- **305**
nium for the metals of the fifth group according to the instructions given in § 196.

d. *Residue IV.* Compare (**299**). **306**

This may contain tin and antimony, perhaps also copper. Proceed as directed (**123**). If the color of the residue was black (oxide of copper), treat the reduced metals according to the instructions given in § 184.

9. *Examination of the Filtrate reserved in* (**291**) *for Metals of the Fourth and Third Groups, especially for Zinc and Chromium.*

a. As we have seen in (**291**), the fluid filtered from the **307**
precipitate produced by hydrosulphuric acid, and temporarily reserved for further examination, has already been mixed with sulphide of ammonium. The addition of this reagent to the filtrate is usually attended with the formation of a precipitate, consisting of sulphide of iron and phosphate of lime, but which may possibly also contain sulphide of zinc. Filter the fluid from this precipitate, and treat the filtrate as directed in (**308**); wash the precipitate with water mixed with some sulphide of ammonium, dissolve by warming with hydrochloric acid, and boil the solution with nitric acid, to convert the protoxide of iron into sesquioxide; add, if necessary, sufficient sesquichloride of iron for carbonate of soda to produce a brownish-yellow precipitate in a sample of the fluid; neutralize almost completely with carbonate of soda, precipitate with carbonate of baryta, and filter; the precipitate contains all the sesquioxide of iron and all the phosphoric acid. Concentrate the filtrate, pre-

cipitate the baryta with dilute sulphuric acid, filter, add to the filtrate ammonia to alkaline reaction, and precipitate with sulphide of ammonium the zinc which may be present. For the further examination of the precipitate, see § 109.

308 *b.* If the analysed substance contained chromium, this will be found in the fluid filtered from the precipitate produced by sulphide of ammonium, since this reagent is incapable of throwing down chromium from liquid containing organic matters. If you wish to ascertain whether chromium is really present, evaporate the filtrate to dryness, mix the residue with 3 parts of nitrate of potassa and 1 part of carbonate of soda, and gradually introduce the mixture into a crucible heated to moderate redness. Allow the fused mass to cool, and, when cold, boil with water: yellow coloration of the fluid shows the presence of alkaline chromate, and accordingly of chromium. For confirmatory tests, see § 141.

II. Method for the Detection of Hydrocyanic Acid.

§ 229.

309 In cases of actual or suspected poisoning with hydrocyanic acid, where it is required to separate that acid from articles of food or from the contents of the stomach, and thus to prove its presence, it is highly necessary to act with the greatest expedition, as the hydrocyanic acid speedily undergoes decomposition. Still this decomposition is not quite so rapid as is generally supposed, and indeed it requires some time before the decomposition of the *whole* of the acid present is effected.*

Although hydrocyanic acid betrays its presence, even in minute quantities, by its peculiar odor, still this sign must never be looked upon as conclusive. On the contrary, to adduce positive proof of the presence of the acid, it is always indispensable to separate it, and to convert it into certain known compounds.

The method of accomplishing this is based upon distillation of the acidified mass, and examination of the distillate for hydrocyanic acid. Now, as the non-poisonous salts, ferro- and ferricyanide of potassium, on distillation, likewise yield

* Thus I succeeded in separating a notable quantity of hydrocyanic acid from the stomach of a man who had poisoned himself with that acid in very hot weather, and whose intestines were handed to me full 36 hours after death.—A dog was poisoned with hydrocyanic acid, and the contents of the stomach, mixed with the blood, were left for 24 hours exposed to an intense summer-heat, and then examined; the acid was still detected.

a distillate containing hydrocyanic acid, it is, of course, indispensable—as *Otto* very properly observes—first to ascertain whether one of these salts may not be present. For this purpose, stir a small portion of the mass to be examined with water, filter, acidify the filtrate with hydrochloric acid, and test a sample of it with sesquichloride of iron, another with sulphate of protoxide of iron. If no blue precipitate forms in either, soluble ferro- and ferricyanides are not present, and you may safely proceed as follows:

Test, in the first place, the reaction of the mass under examination; if necessary, after mixing and stirring it with water. If it is not already strongly acid, add solution of tartaric acid until the fluid strongly reddens litmus paper; introduce the mixture into a retort, and place the body of the retort, with the neck pointing upwards, in an iron or copper vessel, but so that it does not touch the bottom, which should, moreover, by way of precaution, be covered with a cloth; fill the vessel with a solution of chloride of calcium, and apply heat, so as to cause gentle ebullition of the contents of the retort. Conduct the vapors passing over, with the aid of a tight-fitting tube, bent at a very obtuse angle through a *Liebig's* condensing apparatus, and receive the distillate in a small, weighed flask. When about half-an-ounce of distillate has passed over, remove the receiver, and replace it by a somewhat larger flask, also previously tared. Weigh the contents of the first receiver and proceed as follows: **310**

a. Mix one-fourth of the distillate with solution of potassa or soda to strongly alkaline reaction, and then add a small quantity of solution of sulphate of protoxide of iron, mixed with a little sesquichloride of iron. Heat now gently for some minutes and finally supersaturate with dilute hydrochloric acid. If a blue precipitate is formed, it indicates a relatively large amount of hydrocyanic acid; if a bluish-green liquid is obtained from which, on long standing, blue flocks deposit, a small quantity is present. **311**

b. Treat another fourth as directed § 158, 7, to convert the hydrocyanic acid into sulphocyanide of iron. As the distillate might, however, contain acetic acid, do not neglect to add some hydrochloric acid after the sesquichloride of iron, in order to neutralize the adverse influence of the acetate of ammonia. Compare § 114, 8, note. **312**

c. If the experiments *a* and *b* have demonstrated the presence of hydrocyanic acid, and you wish now also to **313**

approximately determine its quantity, continue the distillation, until the fluid passing over contains no longer the least trace of hydrocyanic acid; add one-half of the contents of the second receiver to the remaining half of the contents of the first, mix the fluid with nitrate of silver, then with ammonia until it predominates, and finally with nitric acid to strongly acid reaction. Allow the precipitate which forms to subside, filter on a tared filter, dried at 212° F., wash the precipitate, dry it thoroughly at 212° F., and weigh. Ignite the weighed precipitate in a small porcelain crucible, to destroy the cyanide of silver, fuse the residue with carbonate of soda and potassa—to effect the decomposition of the chloride of silver which it may contain—boil the mass with water, filter, acidify the filtrate with nitric acid, and precipitate with nitrate of silver; determine the weight of the chloride of silver which may precipitate, and deduct the amount found from the total weight of the chloride and cyanide of silver: the difference gives the quantity of the latter; by multiplying the quantity found of the cyanide of silver by 0·2017, you find the corresponding amount of anhydrous hydrocyanic acid; and by multiplying this again by 2—as only one-half of the distillate has been used—you find the total quantity of hydrocyanic acid which was present in the examined mass. Instead of decomposing the precipitate by fusion with an alkaline carbonate it may be treated with zinc and dilute sulphuric acid, and the chlorine determined in the solution after the reduction is complete.

Instead of pursuing this indirect method, you may **314** also determine the quantity of the hydrocyanic acid by the following direct method: Introduce half of the distillate into a retort, together with powdered borax; distil to a small residue, and determine the hydrocyanic acid in the distillate as cyanide of silver. Hydrochloric acid can no longer be present in this distillate, as the soda of the borax retains it in the retort (*Wackenroder*).

III. Method for the Detection of Phosphorus.

§ 230.

Since phosphorus paste has been employed to poison mice, **315** &c., and the poisonous action of lucifer matches has become more extensively known, phosphorus has not unfrequently been resorted to as an agent for committing murder. The chemist is therefore occasionally called upon to examine some

article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state*, or to producing such reactions as will enable him to infer the presence of *free phosphorus;* since the mere finding of phosphorus in form of phosphates would prove nothing, as phosphates invariably form constituents o animal and vegetable bodies.

A. Detection of Unoxidized Phosphorus.

1. Test in the first place the suspected matters as to whether free phosphorus is recognizable by its odor or by its luminosity in the dark, exposing, for this purpose, the materials to the air, as much as is necessary, by rubbing, stirring, or shaking. **316**

2. A portion of the substance is placed, according to the plan of *J. Scherer*,* in a small flask, suspend in it, above the substance, by aid of the loosely fitted cork, a slip of filter paper moistened with neutral solution of nitrate of silver and warm the whole to 85° to 105° Fah. In case the paper is not colored black after some time, unoxidized phosphorus cannot be present, and it is then unnecessary to proceed further by the methods 3 and 4. The operator may go on to (**324**). If, on the other hand, the paper blackens, this is no certain evidence of the presence of phosphorus, because various substances, viz., hydrosulphuric acid (detectable by means of a slip of paper moistened with solution of lead or terchloride of antimony), formic acid, products of putrefaction, &c., may produce the same result. Proceed then with the substance as directed in 3 and 4. **317**

3. The luminosity of phosphorus, of all its characters, furnishes the most striking evidence of its presence in the free state. A large sample of the substance is accordingly examined by the following well-proved and admirable method of *E. Mitscherlich*.† **318**

Mix the substance under examination with water and some sulphuric acid, and subject the mixture to distillation in a flask, A (see Fig. 37). This flask is connected with an evolution tube *b*, and the latter again with a glass cooling or condensing tube, *c c c*, which passes through a perforated cork, *a*, in the bottom of a cylinder, B, into a glass vessel, C. Cold water runs from D, through a stopcock, into a funnel,

* Ann. d. Chem. u. Pharm., 112, 214. † Jour. f. Prakt. Chem., 66, 283.

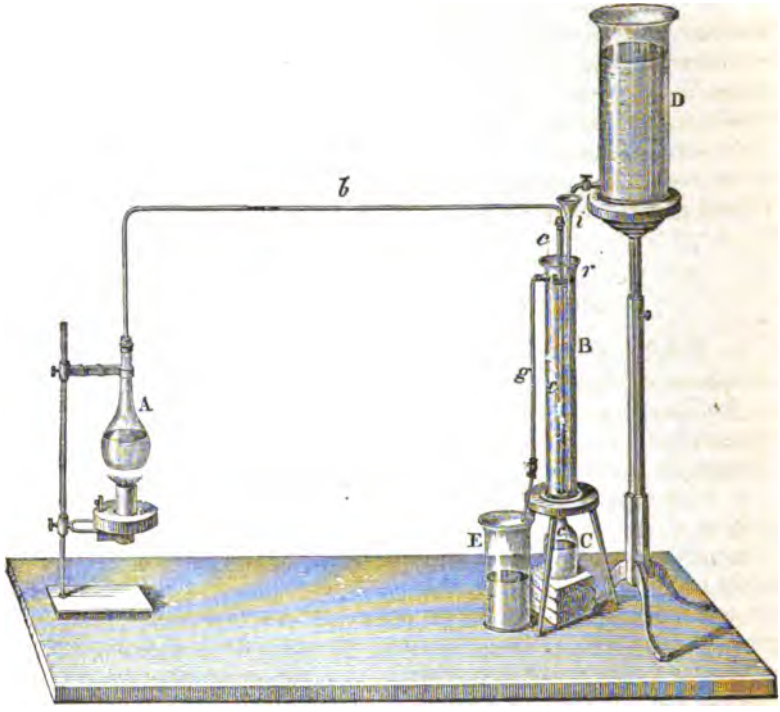

Fig. 87.

i, which extends to the bottom of B; the warmed water flows off through *g*.*

Now, if the substance in A contains phosphorus, there will appear, in the dark, in the upper part of the condensing tube at the point *r*, where the aqueous vapors distilling over enter that part of the tube, a strong luminosity, usually a luminous ring. If you take for distillation 5 oz. of a mixture containing only $\frac{1}{10}$th of a grain of phosphorus, and accordingly only 1 part of phosphorus in 100,000 parts of mixture, you may distil over 3 oz. of it—which will take at least half-an-hour—without the luminosity ceasing; *Mitscherlich*, in one of his experiments, stopped the distillation after half-an-hour, allowed the flask to stand uncorked a fortnight, and then recommenced the distillation: the luminosity was as strong as at first. If the fluid contains substances which prevent the luminosity of phosphorus in general, such as ether, alcohol, or oil of turpentine, no luminosity is observed so long as these

* [Instead of this vertical condenser, the apparatus shown in Fig. 4 may be used.]

substances continue to distil over. In the case of ether and alcohol, however, this is soon effected, and the luminosity accordingly very speedily makes its appearance; but it is different with oil of turpentine, which exercises a lasting preventive influence upon the manifestation of this reaction.

After the termination of the process, globules of phosphorus 319
are found at the bottom of the receiver, C. *Mitscherlich* obtained from 5 oz. of a mixture containing $\frac{1}{5}$ grain of phosphorus, so many globules of that body that the one-tenth part of them would have been amply sufficient to demonstrate its presence. In medico-legal investigations these globules should first be washed with alcohol and then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that they really consist of phosphorus: the remainder, together with a portion of the fluid which shows the luminosity upon distillation, should be sent in with the report.

The experiment should be made in a perfectly dark room, best at night. If it is made in the daytime the room should be darkened by aid of curtains or blinds, so that no reflections whatever from the surfaces of the glass vessels or of the liquids moving in them shall occasion mistakes. It is advisable, even, especially when very minute traces of phosphorus are searched for, to pass the evolution-tube through a screen, at *b*, to prevent such reflections being occasioned by the light of the lamp by which the flask is heated.

The residue of the distillation is further examined according to (**324**) for phosphorous acid. The distillate, also, may be tested in the same manner to confirm the presence of phosphorus, or of phosphorous acid arising from its oxidation.

4. Another sample of the substance may be examined, 320
according to experiments made by *Neubauer* and myself* in the following manner. It is brought into a flask with doubly-perforated stopper, water is added, if necessary, and dilute sulphuric acid to acid reaction. Washed carbonic acid gas† is now slowly conducted through the mixture by means of a glass tube passing through the cork and reaching nearly down to the bottom of the flask. From a short tube above, the current of gas is led through one or two V-formed tubes which contain neutral solution of nitrate of silver. When the flask is filled with carbonic acid it is warmed in a water-bath. The experiment is kept up for several hours. If free phosphorus be present, a portion of it volatilizes unoxidized in the stream of carbonic acid, and on passing into the silver-solution, produces there an insoluble black precipitate of

* Zeitschrift f. Analyt. Chem., 1, 336.

† The apparatus, Fig. 35 (**300**), may be conveniently employed.

phosphide of silver, together with phosphoric acid. Since a black insoluble precipitate may be caused by various volatile reducing agents or by hydrosulphuric acid, its appearance is not proof of the presence of phosphorus, though its non-formation demonstrates conclusively that free phosphorus is absent.

A PRECIPITATE formed in the silver solution in the above 321
experiment is collected on a filter (which has been previously washed with dilute nitric acid and water), and is well washed with water. The phosphide of silver, which may be contained in this precipitate, is detected by the method of *Blondlot*, improved by *Dussard*.* *a* Fig. 38. is an apparatus for evolving hydrogen; *b* is filled with fragments of pumice-stone drenched with concentrated potassa-lye; *c* is a common spring clamp; *d* a clamp that can be nicely adjusted by means of a screw or wedge; *e* is a platinum jet which is kept cool by means of moistened cotton. This platinum jet is essential, since the flame would be colored yellow if burned directly from a glass tube.

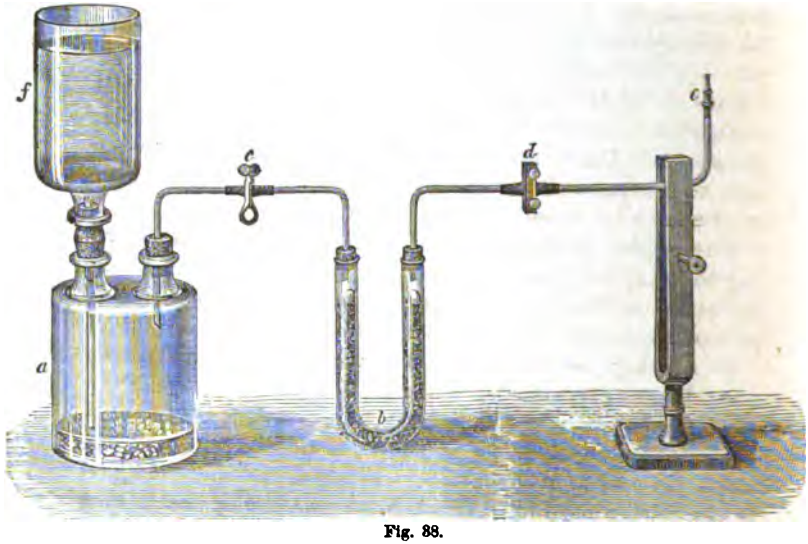

Fig. 88.

At the outset it is needful to test the sulphuric acid and zinc to demonstrate that they yield hydrogen free from phosphuretted hydrogen. For this purpose allow the gas to evolve until air is displaced from the apparatus, then close *c* until the acid has been forced into *f*, then close *d*, open *c*, and lastly open *d*, cautiously inflaming the gas at the jet and properly regulating its issue. If the flame, when examined in a rather dark place, is colorless, exhibits no trace of a green cone in its interior and no emerald-green tinge when a

* Zeitschrift f. Analyt. Chem. 1, 129.

porcelain dish is depressed into it, the hydrogen is pure. After verifying this result by a second trial, the precipitate to be examined is rinsed into *f*, care being taken that it passes completely into *a*, and the flame is again observed as before. In case but a minimum of phosphide of silver be present the green inner cone and emerald-green coloration of the flame will be perceptible.

The SOLUTION filtered from the silver precipitate, is freed from excess of silver by hydrochloric acid, filtered through a well purified filter, strongly concentrated in a porcelain capsule, and finally tested for phosphoric acid by means of molybdate of ammonia or magnesia mixture. **322**

In this manner we have most plainly detected the phosphorus of a common match mixed with a large quantity of putrefied blood, and in presence of those substances which prevent luminosity in the method of *Mitscherlich*.

5. When enough phosphorus is present to weigh, its estimation is practicable by adopting *Scherer's* modification of the process of *Mitscherlich*. The mass, acidified with sulphuric acid, is distilled in an atmosphere of carbonic acid gas. For this purpose it is best to fit into the cork of the flask in which the mixture is distilled, a second tube through which pure carbonic acid may be transmitted into the distilling apparatus, until it is completely filled, when the stream of gas may be cut off and the process continued as usual. The receiver may consist of a flask with a doubly perforated cork, one opening of which passes over the end of the condensing tube, the other carrying a bent glass tube which is connected with a U tube containing solution of nitrate of silver. **323**

When the distillation is finished, globules of phosphorus are found in the receiver, which, after again establishing a gentle stream of carbonic acid, are united by gently heating and then are washed and weighed as described (**319**). The solution poured off from the globules is luminous in the dark, when shaken, though not to the same degree as in *Mitscherlich's* process. The phosphorus in this liquid may be determined, after oxidation, by nitric acid or chlorine, as phosphoric acid; though, only, when the operator is certain that none of the contents of the distilling flask, which usually contain phosphoric acid, have spirted into the condenser. The entire quantity of phosphorus is obtained by adding to that, thus determined, what exists in the U tube. Its contents are treated with nitric acid, the silver thrown down by hydrochloric acid, filtered through a washed filter, concentrated, precipitated as phosphate of ammonia-magnesia, and weighed as phosphate of magnesia.

B. *Detection of Phosphorous Acid.*

In case free phosphorus itself has not been detected by the above methods, it is needful to look for the first product of its oxidation, viz. phosphorous acid. To this end the residue of the distillation (**318**) or (**323**), or also the residue of (**320**) is brought into the apparatus, Fig. 38, and tested as described (**321**), as to any green coloration of the evolved hydrogen. If the phosphorous reaction appears it is sufficient; otherwise, organic matters may have hindered its production. If, therefore, the flame is not colored, the clamp is closed and a U tube containing neutral solution of nitrate of silver is affixed to the apparatus and the gas is allowed to stream slowly through the silver solution for many hours. In presence of phosphorous acid, phosphide of silver is formed, which is filtered off and examined as directed in (**321**). **324**

3. *Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, &c. (Analysis of Ashes.)*

§ 231.

A. Preparation of the Ash.

It is sufficient for the purposes of a qualitative analysis to incinerate a comparatively small quantity of the substance which it is intended to examine for its inorganic constituents; the substance must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be conducted also in a Hessian crucible placed in a slanting position, or, under certain circumstances, even in a small porcelain or platinum dish, over which a wide glass tube (lamp chimney) is supported to increase the access of air. The heat must always be moderate, to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as, *e. g.* the ash of beetroot molasses, it is even advisable to effect, in the first place, complete carbonization, then to boil the charred mass with water, and finally to incinerate the washed and dried residue. For further particulars see *Quantitative Analysis*, 4th Edition, § 250. **325**

B. Examination of the Ash.

As the qualitative analysis of the ash of a vegetable substance is usually undertaken, either as a practical exercise, or for the purpose of determining its general character, and the state or condition in which any given constituent may happen to be present, or also with a view to make, as far as prac- **326**

ticable, an approximate estimation of the respective quantities of the several constituents, it is usually the best way to examine separately; (1) the part soluble in water; (2) the part soluble in hydrochloric acid; and (3) the residue which is insoluble in either menstruum. This can be done the more readily, as the number of bodies to which regard must be had in the analysis is only small, and the several processes may accordingly be expeditiously performed.

a. Examination of the Part Soluble in Water.

Boil the ash with water, filter, and whilst the residue is being washed, examine the solution as follows:—

1. Add to a portion, after heating it, hydrochloric acid in excess, warm, and let the fluid stand at rest. Effervescence indicates CARBONIC ACID, combined with alkalies; odor of hydrosulphuric acid indicates the SULPHIDE of an ALKALI METAL, formed from an alkaline sulphate by the reducing action of the carbon. Turbidity from separation of sulphur, with odor of sulphurous acid, denotes a HYPOSULPHITE (which occurs occasionally in the ash of coal). Filter, if necessary, and add to the filtrate—or to the fluid if no filtration is required—some chloride of barium; the formation of a white precipitate indicates the presence of SULPHURIC ACID. **327**

2. Evaporate another portion of the solution until it is reduced to a small volume, add hydrochloric acid to acid reaction—effervescence indicates the presence of CARBONIC ACID—evaporate now to dryness, and treat the residue with hydrochloric acid and water. The portion left undissolved consists of SILICIC ACID. Filter, add ammonia, chloride of ammonium, and sulphate of magnesia; the formation of a white precipitate indicates the presence of PHOSPHORIC ACID. Instead of this reaction, you may also mix the fluid filtered from the silicic acid with acetate of soda, and then cautiously add, drop by drop, sesquichloride of iron, or you may test with molybdate of ammonia (§ 145). **328**

3. Add to another portion of the solution nitrate of silver as long as a precipitate continues to form; warm gently, and then cautiously add ammonia; if a black residue is left, this consists of sulphide of silver, proceeding from the sulphide of an alkali metal, or from a hyposulphite. Mix the ammoniacal solution now—after previous filtration if necessary—with nitric acid in slight excess, so that phosphate of silver, which at first falls, is redissolved, and only CHLORIDE (iodide and **329**

* To detect the iodine in aquatic plants, dip the plant in a weak solution of potassa (*Chatin*), dry, incinerate, treat with water, and examine the aqueous solution as directed (**257**).

bromide) OF SILVER remains. Filter off the precipitate, which is to be further examined according to (178) and neutralize the filtrate cautiously and exactly with ammonia. If this produces a *bright yellow* precipitate, phosphoric acid is present in the tribasic; if a *white* precipitate, it is present in the bibasic form.

4. Acidify a portion of the solution with hydrochloric acid, 330
and then make it alkaline with ammonia; mix the alkaline fluid with oxalate of ammonia, and let it stand at rest. The formation of a white precipitate indicates LIME. Filter, and mix the filtrate with ammonia and phosphate of soda; the formation of a crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIA. Magnesia is often found in distinctly appreciable lime, only in exceedingly minute quantity, even when alkaline carbonates and phosphates are present.

5. For POTASSA and SODA examine as directed § 200. If magnesia is present, neutralize that portion of the solution intended for detecting alkalies with hydrochloric acid, and separate the magnesia as directed § 199, 2.

6. LITHIA, which is more frequently an ingredient of ashes than has been hitherto suspected, and RUBIDIA, which nearly always accompanies potassa, may be detected by the spectroscope (§ 96), in the residue of alkaline salts.

b. Examination of the Part Soluble in Hydrochloric Acid.

Warm the residue left undissolved by water with hydro- 331
chloric acid*—effervescence indicates CARBONIC ACID, combined with alkaline earths; evolution of chlorine denotes OXIDES OF MANGANESE—evaporate to dryness, and heat a little more strongly, to effect the separation of the silicic acid: moisten the residue with hydrochloric acid and some nitric acid, add water, warm, and filter.

1. Test with hydrosulphuric acid. If this produces any other than a perfectly white precipitate, you must examine it in the usual way. The ashes of plants occasionally contain COPPER; if the plant has been manured with excrements deodorized by nitrate of lead, they may contain LEAD [if with superphosphate made from arsenical oil of vitriol, ARSENIC, *J. Davy*].

2. Mix a portion of the original solution with carbonate of 332
soda, as long as the precipitate formed redissolves upon stirring; then add acetate of soda, and some acetic acid. This produces, in most cases, a white precipitate of PHOSPHATE OF SESQUIOXIDE OF IRON. If the fluid in which this precipitate

* If the residue still contains much carbon, after further incineration.

is suspended is reddish, there is more sesquioxide of iron present than corresponds to the phosphoric acid; if it is colorless, add sesquichloride of iron, drop by drop, until the fluid looks reddish. (From the quantity of the precipitate of phosphate of sesquioxide of iron formed you may estimate the PHOSPHORIC ACID present.) Heat to boiling,* filter hot, and mix the filtrate, after addition of ammonia, with yellow sulphide of ammonium, in a stoppered flask; should a precipitate form, after long standing, examine this according to (**141**) for MANGANESE and ZINC,† and the fluid filtered from it for LIME and MAGNESIA, in the usual way (**330**).

3. To examine for BARYTA and STRONTIA, add dilute sulphuric acid to a portion of the hydrochloric solution, let the mixture stand for a considerable time, and test any precipitate that may form as directed (**254**).

c. Examination of the Residue Insoluble in Hydrochloric Acid.

The residue insoluble in hydrochloric acid contains,

1. The silicic acid, which has separated on treating with hydrochloric acid. **333**

2. Those ingredients of the ash which are insoluble in hydrochloric acid. These are, in most ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stems of cereals and others abounding in silicic acid, that are not completely decomposed by hydrochloric acid.

Boil the washed residue with solution of carbonate of soda in excess, filter hot, wash with boiling water, and test for silicic acid in the filtrate by evaporation with hydrochloric acid (§ 153, 2). **334** If the ash was of a kind to be completely decomposed by hydrochloric acid, the analysis may be considered as finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fluxing. But, if the ash abounded in silicic acid, and it may therefore be supposed that the hydrochloric acid has failed to effect complete decomposition, evaporate half of the residue insoluble in solution of carbonate of soda, with pure solution of soda in excess, in a silver or platinum dish, to dryness. This decomposes the silicates of the ash, whilst but little affecting the sand. Acidify now with hydrochloric acid, evaporate to dryness, &c., and proceed as in (**331**). For the detection of the alkalies use the other half of the residue (**228**).

* If this should fail to decolorize the fluid, add some more acetate of soda.

† [Zinc is found in a species of *violet* growing in the neighborhood of zinc mines.]

SECTION III.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. Additional Remarks to the Preliminary Examination.

To §§ 178–181.

The inspection of the physical properties of a body may, as already stated, § 178, in many cases enable the analyst to draw certain general inferences as to its nature. Thus, for instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a light substance, that it is not a compound of lead, &c.

Inferences of this kind are quite admissible to a certain extent; but if carried too far, they are apt to mislead the operator, by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; however, the experiment in the glass tube gives, in most cases, results more clearly evident, and affords, moreover, the advantage that volatile bodies are less likely to escape detection, and that a more correct and precise notion can be formed of the nature of the heated substance, than exposure on platinum foil or in an iron spoon will permit. To ascertain the products of oxidation of a body, it is sometimes advisable also to heat it in a short glass-tube, open at both ends, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means. (Compare § 159, 6.)

With respect to the preliminary examination by means of the blowpipe, I have to remark that the student must avoid drawing positive conclusions from pyrochemical experiments, until he has acquired some practice in this branch of analytical chemistry. A slight incrustation of the charcoal support, which may *seem* to denote the presence of a certain metal, is not always a *conclusive* proof of the presence of that metal; nor would it be safe to assume the absence of a substance simply because the blowpipe flame fails to effect reduction, or solution of nitrate of protoxide of cobalt fails to impart a color to the ignited mass, &c. The blowpipe reactions are, indeed, in most cases, unerring, but it is not always easy to produce them, and they are moreover liable to suffer modification by accidental circumstances.

The student should never omit the preliminary examination; the notion that this omission will save time and trouble, is very errone-

ous. The beginner may, for example, spend hours in searching for organic acids, when the simple preliminary test would show that they are all absent.

II. Additional Remarks to the Solution of Substances, etc.

To §§ 182–184.

It is a task of some difficulty to fix the exact limit between substances which are soluble in water and those that are insoluble in that menstruum, since the number of bodies which are sparingly soluble in water is very considerable, and the transition from *sparingly* soluble to *insoluble* is very gradual. Sulphate of lime, which is soluble in 430 parts of water, might perhaps serve as a limit between the two classes, since this salt may still be positively detected in aqueous solution, by the delicate reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon platinum foil, to see whether it holds a solid body in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance; in cases of the kind test, in the first place, the reaction of the fluid with litmus papers; in the second place, add to a portion of it a drop of solution of chloride of barium; and lastly, to another portion some carbonate of soda. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not examine it any further for bases or acids; since if the fluid contained any of those bases or acids which principally form sparingly soluble compounds, the chloride of barium and the carbonate of soda would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists, will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination, the student will always do well to examine the solution both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound—an advantage which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in hydrochloric acid or in nitric acid: the phosphates, arsenates, arsenites, borates, carbonates, and oxalates of the earths and metals; and also several tartrates, citrates, malates, benzoates, and succinates; the oxides and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are, indeed, decomposed, if not by dilute, by boiling concentrated hydrochloric

acid ;* but this decomposition gives rise to the formation of insoluble compounds when oxide of silver is present, and of sparingly soluble compounds in the presence of suboxide of mercury and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid has left a residue. But, on the other hand, nitric acid leaves, besides the bodies insoluble in any simple acid, teroxide of antimony, binoxide of tin, binoxide of lead, &c., undissolved, and fails also to effect the complete solution of many other substances, *e. g.* sesquioxide of iron and alumina.

Substances not soluble in water are, therefore, treated as follows: try to dissolve them in dilute or concentrated hydrochloric acid, cold or boiling; if this fails to effect complete solution, try to dissolve a fresh portion in nitric acid; if this also fails, treat the body with aqua regia, which is an excellent solvent, more particularly for metallic sulphides. To examine separately the solution in hydrochloric acid or in nitric acid, on the one hand, and that in nitrohydrochloric acid on the other, is, in most cases, unnecessary. To prepare a nitric or nitrohydrochloric solution is disadvantageous when not necessary, because a hydrochloric solution is much better adapted for precipitation with hydrosulphuric acid. To evaporate an aqua-regia solution for the purpose of removing excess of acid is unadvisable, since volatile chlorides, especially chloride of arsenic, may thus be lost. Use, therefore, no more acid at the outset than is necessary in making the solution.

With regard to the solution of metals and alloys, I have to remark that, upon boiling them with nitric acid, white precipitates will frequently form, although neither tin nor antimony be present. Inexperienced students often confound such precipitates with the oxides of these two metals, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water or not, before he concludes them to consist of tin or antimony.

III. Additional Remarks to the Actual Analysis.

To §§ 185–207.

A. General Review and Explanation of the Analytical Course.

a. Detection of the Bases.

The classification of the bases into six groups, and the methods which serve to detect and isolate them individually, have been fully

* For the exceptions, see § 206.

explained in Part I., Section III. The systematic course of analysis, from § 192 to § 201, is founded upon this classification of the bases; and as a correct apprehension of it is of primary importance, I will here subjoin a brief explanation of the grounds upon which this division rests. Respecting the detection of the several bases individually, I refer the student to the recapitulations and remarks in §§ 95, 102, 106, 115, 121, 126, 130 and 137.

The general reagents which serve to divide the bases into principal groups are—HYDROCHLORIC ACID, HYDROSULPHURIC ACID, SULPHIDE OF AMMONIUM, and CARBONATE OF AMMONIA; this is likewise the order of succession in which they are applied. Sulphide of ammonium performs a *double* part.

Let us suppose we have in solution the whole of the bases, together with arsenious and arsenic acids, and also phosphate of lime—which latter may serve as a type for the salts of the alkaline earths, soluble in acids, and reprecipitated unaltered by ammonia.

Chlorine forms insoluble compounds only with silver and mercury; chloride of lead is sparingly soluble in water. The insoluble subchloride of mercury corresponds to the suboxide of that metal. If, therefore, we add to our solution:

1. *Hydrochloric Acid*,

we remove from it the metallic oxides of the first division of the fifth group, viz. the whole of the OXIDE OF SILVER and the whole of the SUBOXIDE OF MERCURY. From concentrated solutions, a portion of the LEAD may likewise precipitate as chloride; this is, however, immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrosulphuric acid completely precipitates the oxides of the fifth and sixth group from solutions containing a free mineral acid, since the affinity of the metallic radicals of these oxides for sulphur, and that of the hydrogen for oxygen, are sufficiently powerful to overcome the affinity between the metal and the oxygen, and that between the oxide and a strong acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under these circumstances, since those of the first, second, and third group form no sulphur compounds insoluble in water; and the affinity which the metallic radicals of the oxides of the fourth group possess for sulphur, combined with that manifested by hydrogen for oxygen, is not sufficiently powerful to overcome the affinity of the metal for oxygen and of the oxide for a strong acid, IF THE LATTER IS PRESENT IN EXCESS.

If, therefore, after the removal of the oxide of silver and suboxide of mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrosulphuric Acid*,

we remove from it the remainder of the oxides of the fifth, together with those of the sixth group, viz., OXIDE OF LEAD, OXIDE OF MERCURY, OXIDE OF COPPER, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, TEROXIDE OF GOLD, BINOXIDE OF PLATINUM, PROTOXIDE OF TIN, BINOXIDE OF TIN, TEROXIDE OF ANTIMONY, ARSENIOUS ACID, and ARSENIC ACID. All the other oxides remain in solution, either unaltered, or reduced to a lower degree of oxidation, *e. g.* sesquioxide of iron to protoxide; chromic acid to sesquioxide of chromium, &c.

The sulphides corresponding to the oxides of the sixth group combine with basic metallic sulphides (the sulphides of the alkali metals), and form with them sulphur salts soluble in water; while the sulphides corresponding to the oxides of the fifth group do not possess this property, or possess it only to a limited extent.* If, therefore, we treat the whole of the sulphides precipitated by hydrosulphuric acid from an acid solution, with—

3. *Sulphide of Ammonium* (or, in certain cases, *Sulphide of Sodium*),

if necessary, with addition of some sulphur or yellow sulphide of ammonium, the sulphides of mercury, lead, copper, bismuth, and cadmium remain undissolved, whilst the other sulphides dissolve as double compounds of sulphide of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with SULPHIDE OF AMMONIUM (or, as the case may be, SULPHIDE OF SODIUM), and precipitate again from this solution upon the addition of an acid, either unaltered, or, as regards the protosulphide of tin and the tersulphide of antimony, in a state of higher sulphuration—these two compounds taking up sulphur from the yellow sulphide of ammonium. The rationale of this precipitation is as follows:—The acid decomposes the sulphur salt formed. The sulphur base (sulphide of ammonium or sulphide of sodium) transposes with the constituents of the water, forming an oxygen base (oxide of ammonium or soda) and hydrosulphuric acid; the former combines with the acid added, the latter escapes, and the liberated electro-negative sulphide (sulphur acid) precipitates. If the acid is an hydracid, its radical combines with the ammonium, its hydrogen with the sulphur. Sulphur precipitates at the same time, the sulphide of ammonium containing generally an excess of that element. The analyst must bear in mind that this eliminated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The alkalies, the alkaline earths, alumina, and sesquioxide of

* Sulphide of mercury combines with sulphide of potassium and sulphide of sodium, but not with sulphide of ammonium; sulphide of copper dissolves a little in sulphide of ammonium, but not in sulphide of potassium or sulphide of sodium.

chromium have remained in solution, because their sulphur compounds are soluble in water, or because their salts are not affected in the least by hydrosulphuric acid; the sulphides corresponding to the oxides of the fourth group are insoluble in water, and would have been precipitated accordingly by hydrosulphuric acid, but for the free acid present. If, therefore, this free acid is removed, *i. e.*, if the solution is made alkaline, and then treated with hydrosulphuric acid, or, what answers both purposes at once, if

4. *Sulphide of Ammonium*,

is added to the solution,* the sulphides corresponding to the oxides of the fourth group will precipitate: viz., the SULPHIDES OF IRON, MANGANESE, COBALT, NICKEL, and ZINC. But in conjunction with them, ALUMINA, SESQUIOXIDE OF CHROMIUM, and PHOSPHATE OF LIME are thrown down, because the affinity which the oxide of ammonium possesses for the acid of the salt of alumina or of sesquioxide of chromium, or for that which keeps the phosphate of lime in solution, causes the elements of the sulphide of ammonium to transpose with those of the water, thus giving rise to the formation of oxide of ammonium and of hydrosulphuric acid. The former combines with the acid, the latter escapes, being incapable of entering into combination with the liberated oxides or with the phosphate of lime,—the oxides and the lime-salt precipitate.

There remain now in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water, whilst those of the latter are soluble in that menstruum. If, therefore, we now add

5. *Carbonate of Ammonia*,

and some ammonia, in order to prevent the formation of bicarbonates, the whole of the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTA, STRONTIA, and LIME; of magnesia we know that, owing to its disposition to form double compounds with salts of ammonia, it precipitates only in part; and that the presence of an additional salt of ammonia will altogether prevent its precipitation. To guard against any uncertainty arising from this cause, chloride of ammonium is added previously to the addition of the carbonate of ammonia, and thus the precipitation of the magnesia is altogether prevented.

We have now in solution magnesia and the alkalies. The detection of magnesia may be effected by means of phosphate of soda

* After previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrosulphuric acid; and the addition also, if necessary, of chloride of ammonium to prevent the precipitation of magnesia by ammonia.

and ammonia; but its separation requires a different method, since the presence of phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesia is based upon the insolubility of that earth in the pure state. The substance under examination is accordingly ignited in order to expel the salt of ammonia, and the magnesia is then precipitated by means of baryta, the alkalies, together with the newly formed salt of baryta and the excess of the caustic baryta added, remaining in solution. By the addition of carbonate of ammonia, the compounds of baryta are removed from the solution, which now only contains the fixed alkalies, the salt of ammonia formed, and the excess of the salt of ammonia added. If the salts of ammonia are then removed by ignition, the residue consists of the fixed alkalies alone. This method of separating the baryta affords the advantage over that of effecting the removal of that earth by means of sulphuric acid, that the alkalies are obtained in the most convenient form for their subsequent individual detection and isolation, viz., as chlorides. But as carbonate of baryta is slightly soluble in salts of ammonia, and gives, upon evaporation with chloride of ammonium, carbonate of baryta and chloride of barium, it is usually necessary, after the expulsion of the salts of ammonia by ignition, to precipitate it once more with carbonate of ammonia, in order to obtain a solution perfectly free from baryta. Lastly, to effect the detection of the ammonia, a fresh portion of the substance must of course be taken.

b. Detection of the Acids.

Before passing on to the examination for acids and salt radicals, the analyst should first ask himself *which* of these substances may be expected to be present, from the nature of the detected bases and the class to which the substance under examination belongs with respect to its solubility in water or acids, since this will save him the trouble of unnecessary experiments. Upon this point I refer the student to the table in Appendix IV., in which the various compounds are arranged according to their several degrees of solubility in water and acids.

The general reagents applied for the detection of the acids are, for the inorganic acids chloride of barium and nitrate of silver, for the organic acids chloride of calcium and sesquichloride of iron. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether the presence of organic acids must also be looked for. The latter is invariably the case, if the body, when ignited, turns black, owing to separation of carbon.—In the examination for bases the different reagents serve to effect the actual separation of the several groups of bases from each

other; but in the examination for acids they serve simply to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose we have an aqueous solution containing the whole of the acids, in combination with soda, for instance.

Baryta forms insoluble compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; fluoride of barium also is insoluble or, at least, difficultly soluble; all these compounds are soluble in hydrochloric acid, with the exception of sulphate of baryta. If, therefore, to a portion of our neutral or, if necessary, neutralized solution, we add,

1. *Chloride of Barium*,

the formation of a precipitate will denote the presence of at least one of these acids. By treating the precipitate with hydrochloric acid, we learn at once whether sulphuric acid is present or not, as all the salts of baryta being soluble in this menstruum, with the exception of the sulphate, a residue left undissolved by the hydrochloric acid can consist only of the latter salt. When sulphate of baryta is present, the reaction with chloride of barium fails to lead to the positive detection of the whole of the other acids enumerated. For upon filtering the hydrochloric solution of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not always fall down again, being kept in solution by the chloride of ammonium formed. For this reason, chloride of barium cannot serve to effect the actual separation of the whole of the acids named, and except as regards sulphuric acid, we set no value upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, since the non-formation of a precipitate upon its application in neutral or alkaline solutions, proves at once the absence of so considerable a number of acids.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferro- and ferricyanogen, and of the oxide of silver with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid, are insoluble in water. The whole of these compounds are soluble in dilute nitric acid, with the exception of the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, and sulphide of silver. If, therefore, we add to our solution, which, for the reason just now stated, must be perfectly neutral,

2. *Nitrate of Silver*,

and precipitation ensues, this shows at once the presence of one or several of the acids enumerated · chromic acid, arsenic acid, and ·

several others, which form colored salts with silver, may be individually recognised with tolerable certainty by the mere color of the precipitate. By treating the precipitate now with nitric acid, we see whether it contains any of the haloid compounds of silver, or sulphide of silver, as these remain undissolved, whilst all the oxide salts dissolve.—Nitrate of silver fails to effect the complete separation of those acids which form with oxide of silver compounds insoluble in water, from the same cause which renders the separation of acids by chloride of barium uncertain, viz. the ammoniacal salt formed prevents the reprecipitation of several of the salts of silver by ammonia, from the acid solution. Nitrate of silver, besides effecting the separation of chlorine, iodine, bromine, cyanogen, &c., and indicating the presence of chromic acid, &c., serves, like the chloride of barium, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with chloride of barium and with nitrate of silver, indicates therefore at once the further course of the investigation. Thus, for instance, where chloride of barium has produced a precipitate, whilst nitrate of silver has failed to do so, it is not necessary to test for phosphoric acid, chromic acid, boracic acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, *provided always the solution did not already contain salts of ammonia.* The same circumstance is to be considered in case we obtain a precipitate by nitrate of silver, but none by chloride of barium.

Returning now to the supposition which we have assumed here, viz., that the whole of the acids are present in the solution under examination, the reactions with chloride of barium and nitrate of silver would accordingly have demonstrated already the presence of SULPHURIC ACID, and led to the application of the special tests for CHLORINE, BROMINE, IODINE, CYANOGEN, FERROCYANOGEN, FERRICYANOGEN, and SULPHUR;* and there would be reason to test for all the other acids precipitable by these two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained in the course of the present work: the same remark applies to the rest of the inorganic acids, viz., nitric acid and chloric acid.

Of the organic acids, oxalic acid, paratartaric acid, and tartaric acid, are precipitated by chloride of calcium in the cold, in presence of chloride of ammonium; the two former immediately, the latter often only after some time; but the precipitation of citrate of lime is prevented by the presence of salts of ammonia, and ensues only

* For the separation and special detection of these substances, I refer to § 160.

upon ebullition or upon mixing the solution with alcohol; the latter agent serves also to effect the separation of malate of lime from aqueous solutions. If, therefore, we add to our fluid,—

3. *Chloride of Calcium* and Chloride of Ammonium,

OXALIC ACID, PARATARTARIC ACID, and TARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, phosphate of lime, for instance, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids such reactions only as preclude the possibility of confounding the organic acids with the inorganic acids that have been thrown down along with them. For the detection of oxalic acid we select accordingly solution of sulphate of lime, with addition of acetic acid (§ 148); to effect the detection of the tartaric and paratartaric acids, we treat the precipitate produced by chloride of calcium with solution of soda, since the lime-salts of these two acids only are soluble in this menstruum in the cold, but insoluble upon ebullition.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID and MALIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, &c., of lime, and which still contains an excess of chloride of calcium. Sulphate and borate of lime invariably precipitate along with the malate and citrate of lime, if sulphuric acid and boracic acid happen to be present; the analyst must therefore carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is now removed by evaporation, and to the perfectly neutral solution,—

4. *Sesquichloride of Iron*

IS added. This reagent precipitates SUCCINIC ACID and BENZOIC ACID, in combination with sesquioxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods which serve to effect the separation of the several groups from each other, and the individual detection of the various acids, have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

In this section attention will be directed to various points which could not be noticed in the course of analysis, and explanations will be given, in small type, how to proceed when the presence of the *rarer elements* is suspected.

To § 192.

At the commencement of § 192, the analyst is directed to mix neutral or acid aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms, a few drops are sufficient, since the only object in that case is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group, by hydrosulphuric acid. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration that nitric acid also produces precipitates in many cases—in a solution of potassio-tartrate of antimony, for instance—I prefer the use of hydrochloric acid, *i. e.* the complete precipitation by that acid of all that is precipitable by it, for the following reasons:—1. Metals are more readily precipitated by hydrosulphuric acid from solutions acidified with hydrochloric acid, than from those acidified with nitric acid;—2. In cases where the solution contains silver, suboxide of mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these three metals in the form of chlorides;—and 3. This latter form is the best adapted for the individual detection of these three metals when present in the same solution. Besides, the application of hydrochloric acid saves the necessity of examining whether the mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the form of oxide or in that of suboxide. That the lead, if present in large proportion, is obtained partly in the form of a chloride, and partly in the precipitate produced by hydrosulphuric acid in the acid solution, can hardly be thought an objection to the application of this method, as the removal of the larger portion of the lead from the solution, effected at the commencement, will only serve to facilitate the examination for other metals of the fifth and sixth groups.

As already remarked, a basic salt of teroxide of antimony may separate from potassio-tartrate of antimony, for instance, or from some other analogous compound, and precipitate along with the insoluble chloride of silver and subchloride of mercury, and the sparingly soluble chloride of lead. This precipitate, however, is readily soluble in the excess of hydrochloric acid which is subsequently added, and exercises therefore no influence whatever upon the further process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated subchloride of mercury into chloride.

Should bismuth or chloride of antimony be present, the addition of the washings of the precipitate produced by hydrochloric acid

to the first filtrate will cause turbidity, if the amount of free hydrochloric acid present is not sufficient to prevent the separation of the basic salt. This turbidity exercises, however, no influence upon the further process, since hydrosulphuric acid as readily converts these finely-divided precipitates into sulphides, as if the metals were in actual solution.

In the case of alkaline solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction of the fluid combines with the hydrochloric acid, and the bodies originally dissolved in that acid separate. Thus, if the alkali was present in the free state, oxide of zinc, for instance, or alumina, &c., may precipitate. But these oxides redissolve in an excess of hydrochloric acid, whereas chloride of silver would not redissolve, and chloride of lead only with difficulty. If a metallic sulphur salt was the cause of the alkaline reaction, the sulphur acid, *e. g.*, tersulphide of antimony, precipitates upon the addition of the hydrochloric acid, whilst the sulphur base, *e. g.*, sulphide of sodium, transposes with the constituents of the hydrochloric acid, forming chloride of sodium and hydrosulphuric acid. If an alkaline carbonate, a cyanide, or the sulphide of an alkali metal was the cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or hydrosulphuric acid escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of entire groups of bodies.

In solutions which contain alkaline salts of antimonic, tantalic, hyponiobic, molybdic or tungstic acids, hydrochloric acid likewise throws down precipitates. Those yielded by antimonic, tantalic and molybdic acids, dissolve in excess (the tantalic precipitate to an opaline liquid). *Hyponiobic* and *tungstic* acids are, on the contrary, insoluble in excess of hydrochloric acid. The last two acids therefore remain with the precipitate, which may also contain chloride of silver, subchloride of mercury, chloride of lead, and silicic acid. The separation of sulphur, beginning some time subsequent to the addition of hydrochloric acid and attended by the evolution of sulphurous acid, indicates *hyposulphites*.

To §§ 193 AND 194.

To make an analysis in the shortest possible time, the experimenter must accustom himself to carry on several processes at once, and not to stand in idleness during an operation that requires time. Thus, after having procured a hydrosulphuric acid precipitate, instead of waiting until it is completely washed before going further, the analyst may test the first drops of the filtrate with hydrosulphuric acid to make sure that the precipitation is perfect, and such being the case, he may add sulphide of ammonium to learn whether bases of Groups III. and IV. are present, and in their absence carbonate of ammonia may be employed to decide the

presence or absence of alkaline earths. When these experiments are finished, the filtrate will usually be ready to treat with sulphide of ammonium or carbonate of ammonia as the case may require, and the second precipitate may be brought upon a filter while the first is being washed. As soon as the first is washed sufficiently, it may be digested with sulphide of ammonium, while at the same time the second precipitate is washing. In this way, after a little practice, the analyst will learn to occupy his time fully, and will be able to accomplish double the work that would otherwise be possible. [The beginner should not fail to use the necessary means to avoid confusion. For this purpose his precipitates, solutions, &c., should be labelled, especially when several operations are going on side by side or when his products must stand over night. In most cases it is only necessary to write upon the paper cover of the vessel or upon a slip of gummed paper attached to its side, the *marginal number* of the analytical course belonging to the paragraph according to which the solution or precipitate is to be treated on resuming work. No matter how powerful may be one's memory, the habit of labelling will often save from perplexing uncertainty and effect a real economy of time.]

In cases where the analyst has simply to deal with metallic oxides of the sixth group—*e. g.*, teroxide of antimony—and of the fourth or fifth group—*e. g.*, iron or bismuth—he need not precipitate the acidified solution with hydrosulphuric acid, but may, after neutralization, at once add sulphide of ammonium in excess. The sulphide of iron, &c., will in that case precipitate, whilst the antimony, &c., will remain in solution, from which they will, by addition of an acid, at once be thrown down as tersulphide of antimony, &c. This method has the advantage that the fluid is diluted less than is the case where solution of hydrosulphuric acid is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrosulphuric acid gas is conducted into the fluid. The beginner must bear well in mind that he is very liable to fall into error in the precipitation by hydrosulphuric acid, by employing a solution of the latter that is too weak or altogether spoiled, or by adding it in too small quantity, as well as by passing the gas into a solution that is too concentrated or contains *too great an excess* of hydrochloric or nitric acid. Suppose, for instance, that a very strongly acid solution of iron and bismuth is in hand; addition of a little solution of hydrosulphuric acid, or transmission of the gas, produces no precipitate on account of the large excess of acid. It is thence concluded that no base, precipitable by hydrosulphuric acid, is present, and the analyst naturally proceeds to add sulphide of ammonium, and thus obtains sulphide of bismuth, together with the sulphide of iron. On treating this precipitate with dilute hydrochloric acid, a black residue

remains which is at once mistaken for cobalt or nickel. When the beginner has thus lost his way it is very difficult to set himself right again. Acid solutions must therefore be sufficiently diluted, and it must not be neglected to warm them, as otherwise arsenic acid may be overlooked.

On treating acid solutions with hydrosulphuric acid, or on acidifying the sulphide of ammonium in which the hydrosulphuric precipitate has been digested, precipitates are often obtained which so closely resemble pure sulphur that the operator is in doubt whether to test them for metals. In such cases, the precipitate may be washed first with water, then with alcohol, and finally digested with bisulphide of carbon, which takes up sulphur, leaving in a pure state any metallic sulphide.

The precipitate produced by hydrosulphuric acid in acid solutions may contain the sulphides of the following rarer elements: Palladium, rhodium, osmium, ruthenium, iridium,* molybdenum, tellurium, selenium.†

The following cause a separation of sulphur, by oxidizing the hydrogen of the hydrosulphuric acid, viz.: The higher oxides and chlorides of manganese and cobalt, vanadic acid (the liquid becoming blue), nitrous, sulphurous, hyposulphurous, hypochlorous, chlorous, bromic and iodic acids.

On digesting the precipitate with sulphide of ammonium (sulphide of sodium) there pass into solution (with sulphides of antimony, arsenic, &c.), the sulphides of iridium, molybdenum, tellurium, and selenium, while the sulphides of palladium, rhodium, osmium, and ruthenium remain undissolved.

To § 195.

When the precipitate which contains all the sulphides of metals of group VI., viz., tin, antimony, arsenic, tellurium, selenium, molybdenum, gold, platinum, and iridium, is fused with carbonate and nitrate of soda, and the fused mass is treated with cold water, as directed § 195, there pass into solution with arsenic acid, *telluric*, *selenic*, and molybdic acids, while *iridium* remains in the residue, with binoxide of tin, antimonate of soda, gold and platinum.

The mode of detecting the rarer elements in the solution and residue may be gathered from § 138.

To § 196.

Besides the methods described in the systematic course to distinguish between cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results. Add carbonate of soda to the nitric acid solution as long as a pre-

* The platinum metals are not easy to precipitate completely by hydrosulphuric acid. The gas must be passed into the solution a long time with application of a gentle heat.

† Tungsten and vanadium are not found in the precipitate produced by hydrosulphuric acid in acid solution. When the solution is first treated with sulphide of ammonium, and then with hydrochloric or other strong acid in excess, they remain undissolved (as do sulphides of nickel and cobalt), and mixed with the sulphides of groups V. and VI.

cipitate continues to form, then solution of cyanide of potassium in excess, and heat gently. This effects the complete separation of lead and bismuth in the form of carbonates, whilst copper and cadmium are obtained in solution in the form of cyanide of copper and potassium, and cyanide of cadmium and potassium. Lead and bismuth may now be readily separated from one another by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in cyanide of potassium, hydrosulphuric acid in excess, gently heating, and then adding some more cyanide of potassium, in order to redissolve the sulphide of copper which may have precipitated along with the sulphide of cadmium. A residuary yellow precipitate (sulphide of cadmium), insoluble in the cyanide of potassium, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (sulphide of copper) will demonstrate the presence of copper.

If the sulphides of palladium, rhodium, osmium, and ruthenium are suspected in the precipitate containing sulphide of copper, sulphide of bismuth, &c., proceed as follows:

Fuse the precipitate with hydrate and chlorate of potassa, carrying the heat finally to redness. Treat the cooled mass with water. The solution now contains osmate and ruthenate of potassa, and is colored deep yellow by the latter salt. Neutralize cautiously with nitric acid, when *black oxide of ruthenium* separates. Add to the filtrate more nitric acid and distil; *osmic acid* passes over.

The residue undissolved in water is gently ignited in a stream of hydrogen gas (in which process cadmium may volatilize) and cautiously treated with dilute nitric acid which dissolves copper, lead, &c., and leaves behind rhodium and palladium. Aqua regia dissolves *palladium* while *rhodium* remains unaffected. As to the further examination of the metals thus separated, refer to § 127. Mercury may be looked for in a separate portion of the precipitated sulphides.

To § 197.

In case the solution filtered from the hydrosulphuric acid precipitate contains all the elements of groups III. and IV. we obtain, when the solution is treated with chloride and sulphide of ammonium and ammonia in excess, a precipitate in which occur.

a. As sulphides: Cobalt, nickel, manganese, iron, zinc, uranium and [thallium].

b. As oxides: Aluminum, glucinum, thorium, zirconium, yttrium, terbium, erbium, cerium, lanthanum, didymium, chromium, titanium, tantalum and niobium*.

When the rarer elements are suspected, the following course of analysis is in many cases the most satisfactory:

Wash and dry the precipitate, roast it in a porcelain crucible and then fuse it in a platinum crucible with *bisulphate of potassa* for a considerable time. Digest the cooled mass for some time in cold water and filter.

The *residue* which may contain tantalum and niobium, as well as silica and some

* A small quantity of hyponiobic acid, redissolved by hydrochloric acid in the precipitation by that reagent, may be present.

undissolved oxides of iron and chromium, is fused with hydrate and a little nitrate of soda, and digested in soda-lye. Chromate and silicate of soda are dissolved, while tantalate and hyponiobate of soda (which are insoluble in soda-lye) remain with oxide of iron. After removing the excess of soda-lye the residue is treated repeatedly with a very dilute solution of carbonate of soda in which the HYPONIOBATE of soda dissolves much more easily than the TANTALATE. Test further according to § 107, 11 and 12.

The *solution* which contains all the other elements of groups III. and IV. is first treated with hydrosulphuric acid to reduce sesquioxide of iron, then largely diluted and heated for a long time to boiling, a current of carbonic acid being at the same time passed through it. Any precipitate thus produced is to be examined for TITANIC ACID; it may also possibly contain some ZIRCONIA.

The filtrate is concentrated by evaporation with addition of nitric acid and precipitated with ammonia: the washed precipitate is dissolved in hydrochloric acid and again precipitated with ammonia. In this manner ZINC, MANGANESE, NICKEL, COBALT [and THALLIUM]* are obtained almost completely in solution while the earths and other oxides remain in the precipitate. The latter is again dissolved in hydrochloric acid and treated cold with excess of *concentrated solution of potassa*. Chromium, alumina and glucina pass into the solution, while the other earths remain with the oxides of iron and uranium. On diluting the alkaline solution and boiling it for some time the glucina and oxide of chromium are thrown down while ALUMINA remains dissolved and may be precipitated by means of chloride of ammonium.

The precipitate is fused with carbonate and nitrate of soda, and CHROMIC ACID and GLUCINA are separated as directed § 106 for the separation of alumina and chromic acid.

The precipitate which consists of the sesquioxides of iron and uranium and the earths insoluble in potassa, may also under some circumstances, viz. in presence of yttria and oxide of cerium, contain glucina and alumina. [It may likewise consist in part or entirely of alumina and magnesia which are sometimes thrown down together by ammonia in a combination which requires a large excess of chloride of ammonium to prevent its formation, and which is quite insoluble in potassa. Before examining for rare earths resolve this precipitate if possible by repeatedly dissolving in hydrochloric acid and precipitating in presence of chloride of ammonium. If it remain undiminished by this treatment, and if no magnesia be found in the solutions after precipitating by ammonia, proceed as follows]

The precipitate is dissolved in hydrochloric acid, and the excess of acid is mostly removed by evaporation. To the cold solution *carbonate of baryta* is added and the mixture is allowed to stand 4 to 6 hours.

The precipitate thus formed, contains the SESQUIOXIDES OF IRON AND URANIUM, and any ALUMINA that escaped previous precipitation, after dissolving in hydrochloric acid, the uranium is removed from the iron and alumina by an excess of carbonate of ammonia.

The liquid filtered from the precipitate by carbonate of baryta is freed from baryta by a slight excess of sulphuric acid, brought to a small bulk by evaporation, exactly or at least very nearly neutralized by means of potassa (the reaction should be acid rather than alkaline), and crystals of neutral *sulphate of potassa* are added, after

* [In the solution THALLIUM may be detected by the yellow precipitate it yields with iodide of potassium, or by the reaction with bichloride of platinum (confirm by the flame test and spectroscope). It may be separated from all the other bases of the fourth group by boiling the solution with carbonate of soda (if ammonia salts are present until these are decomposed and ammonia completely dissipated) carbonate of thallium remains in the solution especially while hot, and all the other bases are converted into insoluble carbonates or oxides.]

which the liquid is boiled a short time and then left at rest for 12 hours. Any precipitate is filtered off and washed with a solution of sulphate of potassa.

The filtrate contains that portion of the glucina which may have escaped solution by potassa, also yttria (together with erbia and terbia). These substances are precipitated by ammonia, and may then be easily separated by treating with a concentrated warm solution of *oxalic acid*, in which the GLUCINA is soluble, whilst the oxalates of YTTRIA and of ERBIA and TERBIA are left undissolved. Now boil the precipitate of the double sulphates of zirconia, &c., and potassa repeatedly in water, with addition of some hydrochloric acid, which will dissolve the THORIA and the OXIDES OF CERIUM, LANTHANUM and DIDYMIUM, leaving the sulphate of ZIRCONIA and potassa undissolved. The thoria and the oxides of cerium, &c., may then be precipitated from the solution by ammonia, and tested by the reactions described in § 107.

To §§ 198—201.

The fluid filtered from the precipitate produced by sulphide of ammonium may not only contain the alkaline earths and the alkalies, but some nickel, and also vanadic acid and that portion of the tungstic acid which has been left unprecipitated by hydrochloric acid. The nickel, the vanadic acid, and the tungstic acid, are present as sulphides dissolved in excess of sulphide of ammonium; they are thrown down in that form by just acidifying the fluid with hydrochloric acid. Filter the precipitate, wash, dry, fuse with carbonate of soda and nitrate of potassa, and treat the fused mass with water; this will dissolve the vanadate and tungstate of potassa, leaving the PROTOXIDE OF NICKEL undissolved. From this solution the VANADIC ACID may be separated by means of solid chloride of ammonium, the TUNGSTIC ACID by evaporating with hydrochloric acid and treating the residue with water. The two acids may then be examined as directed § 116, *b*, and § 138, *c*.

For the detection of lithium, cæsium, and rubidium, I refer to the analysis of mineral waters (**258**) and (**259**).

To § 206.

If the rarer elements are taken into account, the number of bodies which are left undissolved by treating a substance under examination with water, hydrochloric acid, nitric acid, and aqua regia, is much enlarged. The following bodies, more especially, are either altogether, or in the ignited state, or in certain combinations, insoluble or slowly and sparingly soluble in acids:

Glucina, thoria, and zirconia; the oxides of cerium, lanthanum, and didymium; titanic acid and tantalic acid; hyponiobic acid and niobic acid; molybdic acid and tungstic acid; rhodium, iridium, osmio-iridium, ruthenium.

When you have, in the systematic course of analysis, arrived at (**208**), fuse the substance, free from silver, lead, and sulphur, with carbonate of soda and some nitrate of potassa, extract the fused mass repeatedly with hot water, and, if a residue is left, fuse this some time, in a silver crucible, with hydrate of potassa and nitrate of potassa, and again treat the fused mass repeatedly with water. The alkaline solutions, which may be examined separately or together, may contain glucina, a portion of the titanic acid, the tantalic acid, the niobic acids, the molybdic acid, the tungstic acid, the osmic and ruthenic acids, and a portion of the iridium present.

If the residue left undissolved by the preceding operation is fused with acid sulphate of potassa, and the fused mass treated with water, the thoria and zirconia, the oxides of cerium, the remainder of the titanic acid, and the rhodium may dissolve. A residue left by this operation may consist of platinum metals that have escaped decomposition by fluxing, and had best be mixed with chloride of sodium, and ignited in a stream of chlorine.

With respect to the separation and individual detection of the several elements that have passed into the different solutions, the requisite directions and instructions have been given in the third section of Part I., and in the additional remarks to §§ 192—201.

To § 207.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes a difficult task even to ascertain whether we have really a cyanide before us or not. However, if the reactions of the substance under examination upon ignition (8) be carefully observed, and also whether upon boiling with hydrochloric acid any odor of hydrocyanic acid is emitted (35), the presence or absence of a cyanide will generally not long remain a matter of doubt.

It must above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes; viz. they are either SIMPLE CYANIDES, or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other analogous compound radical.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, &c., to which indeed the method described § 207 more exclusively refers, suffer by acids such complicated decompositions that their analysis by means of acids is a task not so easily accomplished. Their decomposition by potassa or soda is far more simple. The alkali yields its oxygen to the metal combined with the ferrocyanogen, &c., the oxide thus formed precipitates, and the reduced potassium or sodium forms with the liberated radical soluble ferrocyanide, &c., of potassium or sodium. But several oxides are soluble in an excess of potassa, as, *e. g.*, oxide of lead, oxide of zinc, &c. If, therefore, the double ferrocyanide of zinc and potassium, for instance, is boiled with solution of caustic potassa, it dissolves completely in that menstruum, and we may assume that the solution contains ferrocyanide of potassium and oxide of zinc dissolved in potassa. Were we to add an acid to this solution, we should of course simply re-obtain the original precipitate of the double ferrocyanide of zinc and potassium, and the experiment would consequently be of no avail. To prevent this failure, we conduct hydrosulphuric acid into the solution in potassa, but only until the precipitable oxides are completely thrown down, and not until the solution smells of sulphuretted hydrogen. This serves to convert into sulphides all the heavy metals which the potassa holds in solution as oxides. Those sulphides which are insoluble in potassa, such as sulphide of lead, sulphide of zinc, &c., precipitate, whilst those which are soluble in alkaline sulphides,

such as bisulphide of tin, tersulphide of antimony, &c., remain in solution. To effect the detection of these also, the fluid is now acidified with nitric acid, and, if necessary, hydrosulphuric acid is conducted into the solution. (The liquid must be diluted before adding the nitric acid, and too great an excess of the last must be avoided, as, otherwise, the solution may acquire a blue color from decomposition of hydroferrocyanic acid set at liberty by the nitric acid.)

The fluid filtered from the precipitated oxides and sulphides accordingly always contains the cyanogen as ferrocyanide, &c., of potassium—provided, of course, the analyzed compound is really a double ferrocyanide, &c. From most of these compounds—ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium—the cyanogen partly separates as hydrocyanic acid, upon boiling the solutions with sulphuric acid, and may thus be readily detected by this means, should the direct way of detecting the radicals not succeed. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and the analyst is accordingly directed to effect the detection of the compound radical in that salt by means of solution of nickel, manganese, zinc, &c. By fusion with nitrate of potassa, all these double compounds suffer decomposition, cobalticyanide of potassium not excepted. The fusion of these double compounds with nitrate of potassa should be preceded by evaporation with an excess of nitric acid, to prevent the occurrence of explosions. Caution is highly advisable in this operation.

If you simply wish to examine for bases in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, drench it in the state of powder with concentrated sulphuric acid diluted with a little water, and heat in a platinum vessel so long and so highly as is needful to expel nearly all the free sulphuric acid. The residue now consists of sulphates which are dissolved in water and in hydrochloric acid for further analysis. *H. Rose.*[*]

[*] Zeitschrift für Analytische Chem. 1, 194.

APPENDIX.

I.

Deportment of the most important Medicinal Alkaloids with Reagents, and Systematic Method of effecting the Detection of these Substances.

§ 232.

The detection and separation of the vegeto-alkalies, or alkaloids, is a task of far greater difficulty than that of most of the inorganic bases. Although this difficulty is in some measure owing to the circumstance that scarcely one of the compounds which the alkaloids form with other substances is absolutely insoluble or particularly characterized by its color or any striking property, yet the principal cause of it must be ascribed to the want of accurate and minute investigations of the salts and other compounds of the alkaloids, and of the products of their decomposition. We consequently generally see and apprehend the reactions only in their external manifestation, but without being able to connect them with the causes producing them, which makes it impossible to understand all the conditions which may exercise a modifying influence.

Although, therefore, in the present imperfect state of our knowledge of these bodies, an attempt to define their deportment with reagents, and base thereon a method of effecting their separation or, at least, their individual detection in presence of each other, must of necessity fall very short of perfection, yet, having made a great many experiments on the nature and deportment of these substances, I will attempt here, for the benefit of young chemists, and more particularly pharmaceutists, to describe in some measure the reactions which the most important of the alkaloids manifest with other bodies, and lay down a systematic method of effecting their individual detection.

The classification of the alkaloids into groups which I have adopted is based upon their deportment with certain general reagents. I have verified by numerous experiments the whole of the reactions described in the succeeding paragraphs.

Recent investigations have shown that several of the alkaloids,

in the state in which they are obtained by the usual methods of preparing them, and in which they occur in commerce or are used in pharmacy, must not be looked upon as simple organic bodies, but as consisting of several, often even of many, very closely allied alkaloids. Thus, for instance, common narcotine contains three or four homologous bases; thus SCHÜTZENBERGER has produced from so-called brucia, by fractional crystallization, ten alkaloids, analogous in form of crystallization and in deportment with nitric acid, but differing in composition and in solubility in water. As these varieties have not as yet been studied with regard to their reactions, I have of course been obliged to disregard them altogether in the subjoined course of analysis, which therefore must be held to refer simply to the vegeto-alkalies in the pure state, such as they have hitherto been assumed to exist.

I. VOLATILE ALKALOIDS.

The volatile alkaloids are fluid at the common temperature, and may be volatilized in the pure state as well as when mixed with water. They are accordingly obtained in the distillate when their salts are distilled with strong fixed bases and water. Their vapors, when brought in contact with those of volatile acids, form a white cloud.

1. NICOTINA, or NICOTINE (C_{10} H_7 N).

§ 233.

1. Nicotina, in its pure state, forms a colorless, oily liquid, of 1·048 sp. gr.; the action of air imparts a yellowish or brownish tint to it. It boils at 482° F., suffering, however, partial decomposition in the process; but, when heated in a stream of hydrogen gas, it distils over unaltered, between 212° and 392° F. It is miscible in all proportions with water, alcohol, and ether.

Nicotina has a peculiar, disagreeable, somewhat ethereal, tobacco-like odor, an acrid, pungent taste, and very poisonous properties. Dropped on paper, it makes a transparent stain, which slowly disappears; it turns turmeric-paper brown, and reddened litmus-paper blue. Concentrated aqueous solution of nicotina shows these reactions more distinctly than the alkaloid in the pure state.

2. Nicotina has the character of a pretty strong base; it precipitates metallic oxides from their solutions, and forms salts with acids. The salts of nicotina are freely soluble in water and alcohol, insoluble in ether; they are inodorous, but taste strongly of tobacco; part of them are crystallizable. Their solutions, when distilled with solution of potassa, give a distillate containing nicotina. By neutralizing this with oxalic acid, and evaporating, oxalate of nicotina is produced, which may be freed from any ad-

mixture of oxalate of ammonia, by means of spirit of wine, in which the former salt is soluble, the latter insoluble.

3. If an aqueous solution of nicotina, or a solution of salt of nicotina mixed with solution of soda or potassa, is shaken with *ether*, the nicotina is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass, the nicotina remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odor.

4. *Bichloride of platinum* produces in aqueous solutions of nicotina whitish-yellow flocculent precipitates. On heating the fluid containing the precipitate, the latter dissolves, but upon continued application of heat it very speedily separates again in form of an orange-yellow, crystalline, heavy powder, which, under the microscope, appears to be composed of roundish crystalline grains. If a rather dilute solution of nicotina, supersaturated with hydrochloric acid, is mixed with bichloride of platinum, the fluid at first remains clear; after some time, however, the double salt separates in small crystals (oblique, four-sided prisms), clearly discernible with the naked eye.

5. *Terchloride of gold* produces a reddish-yellow flocculent precipitate, sparingly soluble in hydrochloric acid.

6. Solution of *iodine in iodide of potassium* and water, when added in small quantity to an aqueous solution of nicotina, produces a yellow precipitate, which after a time disappears. Upon further addition of iodine solution, a copious kermes-colored precipitate separates; but this also disappears again after a time.

7. Solution of *tannic acid* produces a copious white precipitate, which redissolves upon addition of hydrochloric acid.

8. If an aqueous solution of nicotina is added to a solution of *chloride of mercury* in excess, an abundant, flocculent, white precipitate is formed. If solution of chloride of ammonium is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

2. Conia, or Conine (C_{16} H_{15} N).

§ 234.

1. Conia forms a colorless oily liquid, of 0·87 sp. gr.; the action of the air imparts to it a brown tint. In the pure state it boils at about 392° F.; when heated in a stream of hydrogen gas, it distils over unaltered; but when distilled in vessels containing air, it turns brown and suffers partial decomposition; with aqueous vapors it distils over freely. It dissolves sparingly in water, 100 parts of water of the common temperature dissolving 1 part of conia. The solution turns turbid on warming. Conia is miscible in all propor-

tions with alcohol and ether. The aqueous and alcoholic solutions manifest strong alkaline reaction. Conia has a very strong, pungent, repulsive odor, which affects the head, a most acrid and disagreeable taste, and very poisonous properties.

2. Conia is a strong base; it accordingly precipitates metallic oxides from their solutions, in a similar way to ammonia, and forms salts with acids. The salts of conia are soluble in water and in spirit of wine, but nearly insoluble in ether. Hydrochlorate of conia crystallizes readily; the smallest quantity of this base, brought in contact with a trace of hydrochloric acid, yields almost immediately a corresponding quantity of non-deliquescent rhombic crystals (Th. Wertheim). The solutions of the salts of conia turn brownish upon evaporation, with partial decomposition of the conia. The dry salts of conia do not smell of the alkaloid; when moistened, they smell only feebly of it; but upon addition of solution of soda, they at once emit a strong conia odor. When salts of conia are distilled with solution of soda, the distillate contains conia. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with spirit of wine, the oxalate of conia formed is dissolved, whilst any oxalate of ammonia that may be present is left undissolved. As conia is only sparingly soluble in water, and dissolves with still greater difficulty in solutions of alkalies, a concentrated solution of a salt of conia turns milky upon addition of solution of soda. The minute drops which separate unite gradually, and collect on the surface.

3. If an aqueous solution of a salt of conia is shaken with *solution of soda* and *ether*, the conia is dissolved by the ether. If the latter is then allowed to evaporate on a watch-glass, the conia is left in yellowish-colored oily drops.

4. *Concentrated nitric acid* imparts a fine blood-red tint to conia; *sulphuric acid*, a purple-red color, which subsequently turns to olive-green.

5. *Terchloride of gold* produces a yellowish-white precipitate, insoluble in hydrochloric acid; *chloride of mercury*, a copious white precipitate, soluble in hydrochloric acid. *Bichloride of platinum* does not precipitate aqueous solutions of salts of conia, the conia compound corresponding to ammonia-bichloride of platinum being insoluble in spirit of wine and ether, but soluble in water.

6. To solution of *iodine in iodide of potassium* and water, and to solution of *tannic acid*, conia comports itself the same as nicotina.

7. *Chlorine water* produces in a mixture of water and conia a strong, white turbidity.

8. If an aqueous solution of conia is mixed with a solution of *albumen*, the albumen coagulates. Aniline is the only other volatile vegeto-alkali which shows this reaction.

The volatile alkaloids are easily recognised when pure; the great object of the analyst must accordingly always be to obtain them in that state. The way of effecting this is the same for nicotina as for conia, and has already been given in the foregoing paragraphs, viz., to distil with addition of solution of soda, neutralize with oxalic acid, evaporate, dissolve in alcohol, evaporate the solution, treat the residue with water, add solution of soda, shake the mixture with ether, and let the latter evaporate spontaneously. Conia is distinguished from nicotina chiefly by its odor, its sparing solubility in water, and its comportment with chlorine water, and bichloride of platinum.

II. Non-volatile Alkaloids

The non-volatile alkaloids are solid, and cannot be distilled over with water.

First Group.

Non-volatile Alkaloids which are precipitated by Potassa or Soda from the Solutions of their Salts, and redissolve readily in an Excess of the Precipitant.

Of the alkaloids of which I propose to treat here, *one* only belongs to this group, viz.,

Morphia, or Morphine (C_{34} H_{19} N O_6 = Mo).

§ 235.

1. Crystallized morphia ($\dot{M}o$ + 2 aq.) usually appears in the form of colorless, brilliant four-sided prisms, or, when obtained by precipitation, as a white crystalline powder. It has a bitter taste, and dissolves very sparingly in cold, but somewhat more readily in boiling water. Of cold alcohol it requires about 90 parts by weight for solution; of boiling alcohol from 20 to 30 parts. The solutions of morphia in alcohol as well as in hot water manifest distinctly alkaline reaction. This alkaloid is nearly insoluble in ether; it dissolves in amyl-alcohol in the cold, but more freely with the aid of heat. At a moderate heat the crystallized morphia loses the two equivalents of water.

2. Morphia neutralizes acids completely, and forms with them the salts of morphia. These salts are readily soluble in water and in spirit of wine, but insoluble in ether and amyl-alcohol; their taste is disagreeably bitter. Most of them are crystallizable.

3. *Potassa* and *ammonia* precipitate from the solutions of salts of morphia—generally only after some time—$\dot{M}o$ + 2 aq., in the form of a white crystalline powder. Stirring and friction on the sides of the vessel promote the separation of the precipitate, which

redissolves with great readiness in an excess of potassa, but more sparingly in ammonia. It dissolves also in chloride of ammonium and, though with difficulty only, in carbonate of ammonia.

4. *Carbonate of potassa and carbonate of soda* produce the same precipitate as potassa and ammonia, but fail to redissolve it upon addition in excess. Consequently if a fixed alkaline bicarbonate is added to a solution of morphia in caustic potassa, or if carbonic acid is conducted into the solution, $\dot{M}o + 2$ aq. separates,—especially after previous ebullition—in the form of a crystalline powder. A more minute inspection, particularly through a magnifying glass, shows this powder to consist of small acicular crystals; seen through a glass which magnifies 100 times, these crystals present the form of four-sided prisms.

5. *Bicarbonate of soda and bicarbonate of potassa* speedily produce in solutions of neutral salts of morphia a precipitate of hydrated morphia, in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of salts of morphia in the cold.

6. The action of strong *nitric acid* upon morphia or one of its salts, in the solid state or in concentrated solutions, produces a fluid varying from red to yellowish-red. Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon heating they acquire a yellow tint.

7. If morphia or a compound of morphia is treated with pure concentrated *sulphuric acid*, and heat applied, a colorless solution is obtained; if, after cooling, 8 to 20 drops of *sulphuric acid mixed with some nitric acid** are added, and 2 or 3 drops of water, the fluid acquires a violet-red coloration (gentle heating promotes the reaction); and if from 4 to 6 clean lentil-sized fragments of *binoxide of manganese* are now added, or a fragment of *chromate of potassa* (Otto), the fluid acquires an intense mahogany-brown color. If the fluid is then diluted with 4 parts of water, properly cooled in a test tube, and ammonia added until the reaction is *almost* neutral, a dirty-yellow color makes its appearance, which turns brownish red upon supersaturation with ammonia, without depositing an appreciable precipitate (J. Erdmann).

8. *Neutral sesquichloride of iron* imparts to neutral solutions of salts of morphia a beautiful dark blue color, which disappears upon the addition of an acid. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will appear clouded and less distinct.

9. If *iodic acid* is added to a solution of morphia or of a salt of morphia, iodine separates. In concentrated aqueous solutions the

* Mix 6 drops of nitric acid of 1·25 sp. gr. with 100 cubic centimetres of water, and add 10 drops of this mixture to 20 grammes of pure concentrated sulphuric acid.

separated iodine appears as a kermes-brown precipitate, whilst to alcoholic and dilute aqueous solutions it imparts a brown or yellowish-brown color. The addition of starch-paste to the fluid, no matter whether made before or after that of the iodic acid, considerably heightens the delicacy of the reaction, since the blue tint of the iodide of starch remains still perceptible in exceedingly dilute solutions, which is not the case with the brown color imparted by iodine. As other nitrogenous bodies (albumen, caseïne, fibrine, &c.) likewise reduce iodic acid, this reaction has only a relative value; however, if *ammonia* is added after the iodic acid, the fluid becomes colorless if the separation of iodine has been caused by other substances, whilst the coloration becomes much more intense if it is owing to the presence of morphia (LEFORT).*

SECOND GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY BICARBONATE OF SODA EVEN FROM ACID SOLUTIONS, if the latter are not diluted in a larger proportion than 1 : 100; Narcotina, Quina, Cinchonia.

a. NARCOTINA, or NARCOTINE ($C_{46}H_{25}NO_{14} = \dot{N}a$).

§ 236.

1. Crystallized narcotina ($\dot{N}a$ + aq.) appears usually in the form of colorless, brilliant, right rhombic prisms, or, when precipitated by alkalies, as a white, loose, crystalline powder. It is insoluble in water. Alcohol and ether dissolve it sparingly in the cold, but somewhat more readily upon heating. Solid narcotina is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotina does not alter vegetable colors. At 338° F. it fuses, with loss of 1 eq. of water.

2. Narcotina dissolves readily in acids, combining with them to salts. These salts have invariably an acid reaction. Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even upon simple evaporation. Most of the salts of narcotine are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste.

* LEFORT (Zeitschrift f. Anal. Chem. I., 134) recommends the following method for the detection of small quantities of morphia: moisten strips of very white unsized paper with the morphia solution, dry, and repeat the operation several times, so as to ensure absorption by the paper of a tolerably large quantity of the fluid; the dried paper contains the morphia in the solid state, most finely divided. Nitric acid, sesquichloride of iron, and iodic acid and ammonia will readily and with positive distinctness show the characteristic reactions on paper so prepared.

3. *Pure alkalies*, and *alkaline carbonates* and *bicarbonates*, immediately precipitate from the solutions of salts of narcotine $\overset{+}{Na}$ + aq. in the form of a white powder, which, seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles. The precipitate is insoluble in an excess of the precipitants. If solution of narcotina is mixed with ammonia, and ether added in sufficient quantity, the narcotine which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated on a watch-glass, the residue is seen, upon inspection through a lens magnifying a hundred times, to consist of small, distinct, elongated, and lance-shaped crystals.

4. *Concentrated nitric acid* dissolves narcotine to a colorless fluid, which acquires a pure yellow tint upon application of heat.

5. If a small quantity of pure narcotine is treated with from 4 to 6 drops of pure *concentrated sulphuric acid*, no coloration is observed, not even on the application of a gentle heat, or, at least, the heated fluid acquires only a barely perceptible yellow tint, but upon adding now, after cooling, from 8 to 20 drops of sulphuric acid mixed with a little *nitric acid* (§ 235, 7) and 2 or 3 drops of water, the fluid acquires an intense red color. Addition of binoxide of manganese does not materially change the color. If, after dilution, *ammonia* is added to *nearly* neutral reaction, the color becomes less intense, in consequence of the dilution. Addition of ammonia in excess produces a copious dark brown precipitate (J. Erdmann).

6. If the solution of a salt of narcotine is mixed with *chlorine water*, it acquires a yellow color, slightly inclining to green: if ammonia is then added, a much more intensely colored yellowish-red fluid is obtained.

7. If narcotine or one of its salts is dissolved in an excess of dilute *sulphuric acid*, some finely levigated *binoxide of manganese* added, the mixture heated to boiling, and kept in ebullition for the space of several minutes, the narcotine absorbs oxygen and is converted into opianic acid, cotarnine (a base soluble in water), and carbonic acid. Ammonia will now of course fail to precipitate narcotine from the filtrate.

b. Quina, or Quinine ($C_{40}H_{24}N_2O_4=\overset{+}{Q}$).

§ 237.

1. Crystallized quina ($\overset{+}{Q}$ + 6 aq.) appears either in the form of fine crystalline needles of silky lustre, which are frequently aggregated into tufts, or as a loose white powder. It is sparingly soluble

in cold, but somewhat more readily in hot water. It is readily soluble in spirit of wine, both cold and hot, but less so in ether. The taste of quina is intensely bitter; the solutions of quina manifest alkaline reaction. Upon exposure to heat it loses the 6 eq. of water.

2. Quina neutralizes acids completely. The salts taste intensely bitter; most of them are crystallizable, difficultly soluble in cold, readily soluble in hot water and in spirit of wine. The acid salts dissolve very freely in water; the solutions reflect a bluish tint. If a cone of light is thrown into them, by means of a lens either horizontally or vertically, a blue cone of light is seen even in highly dilute solution.

3. *Potassa, ammonia*, and the neutral *carbonates of the alkalies* produce in solutions of salts of quina (if they are not too dilute) a white, loose, pulverulent precipitate of hydrated quina, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of an aggregate of crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of potassa, but more so in ammonia. It is hardly more soluble in fixed alkaline carbonates than in pure water. If a solution of quina is mixed with ammonia, ether added, and the mixture shaken, the quina which has separated upon the addition of the ammonia, redissolves in the ether, and the clear fluid presents two distinct layers. In this point quina differs essentially from cinchonia; by means of this reaction, the former may therefore be readily detected in presence of the latter, and separated from it.

4. *Bicarbonate of soda* also produces both in neutral and acid solutions of salts of quina a white precipitate. In acidified solutions containing 1 part of quina to 100 parts of acid and water, the precipitate forms immediately; if the proportion of the quina to the acid and water is as 1 : 150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is as 1 : 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more complete the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quina to a colorless fluid, turning yellowish upon application of heat.

6. The addition of *chlorine water* to the solution of a salt of quina fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green color. If, after the addition of the chlorine water, some solution of *ferrocyanide of potassium* is added, then

a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid* to the red fluid, the color vanishes, but reappears afterwards upon cautious addition of ammonia. (O. LIVONIUS, communicated in a letter to the author; A. VOGEL.)

7. *Concentrated sulphuric acid* likewise dissolves pure quina and pure salts of quina to a colorless or very faint yellowish fluid; application of a gentle heat turns the fluid yellow, application of a stronger heat brown. Sulphuric acid containing an admixture of nitric acid dissolves quina to a colorless or very faint yellowish fluid.

8. As regards HERAPATH'S quinine reaction, based upon the polarizing properties of sulphate of iodide of quinine, I refer to *Phil. Mag.* vi. 171.

c. CINCHONIA, or CINCHONINE ($C_{40}H_{24}N_2O_2 = \overset{+}{C}i$).

§ 238.

1. Cinchonia appears either in the form of transparent, brilliant, four-sided prisms, or fine white crystalline needles, or if precipitated from concentrated solutions, as a loose white powder. At first it is tasteless, but after some time the bitter taste of the bark becomes perceptible. It is nearly insoluble in cold water, and dissolves only with extreme difficulty in hot water; it dissolves sparingly in cold dilute spirit of wine, more readily in hot spirit of wine, and the most freely in absolute alcohol. From hot alcoholic solutions the greater portion of the dissolved cinchonia separates upon cooling in a crystalline form. Solutions of cinchonia taste bitter, and manifest alkaline reaction. Cinchonia is insoluble in ether.†

2. Cinchonia neutralizes acids completely. The salts have the bitter taste of the bark; most of them are crystallizable: they are generally more readily soluble in water and in spirit of wine than the corresponding quina compounds. Ether fails to dissolve them.

3. Cinchonia, when heated cautiously, fuses at first without loss of water; subsequently white fumes arise which, like benzoic acid, condense upon cold substances, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long brilliant prisms are obtained (HLASIWETZ).

4. *Potassa*, *ammonia*, and the *neutral carbonates of the alkalies* produce in solutions of salts of cinchonia a white loose precipitate

* Acetic acid answers the purpose best.

† The cinchonia of commerce usually contains in admixture another alkaloid, called cinchotina, which is soluble in ether. This alkaloid crystallizes in large rhomboidal crystals of brilliant lustre, which fuse at a high temperature, and cannot be sublimed even in a stream of hydrogen gas (HLASIWETZ).

of CINCHONIA, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even though viewed through a lens magnifying 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears under the microscope to consist of distinct crystalline needles aggregated into star-shaped tufts.

5. *Bicarbonate of soda* and *bicarbonate of potassa* precipitate cinchonia in the same form as in 4, both from neutral and acidified solutions of cinchonia salts, but not so completely as the simple carbonates of the alkalies. Even in solutions containing 1 part of cinchonia to 200 of water and acid, the precipitate forms immediately; its quantity increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonia to a colorless fluid, which upon application of heat first acquires a brown, and finally a black color. Addition of some nitric acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, turns finally black.

7. The addition of *chlorine water* to the solution of a salt of cinchonia fails to impart a color to the fluid; if ammonia is now added, a yellowish-white precipitate is formed.

8. If the solution of a cinchonia salt containing only very little or no free acid, is mixed with ferrocyanide of potassium, a flocculent precipitant of ferrocyanide of cinchonia is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic (CH. DOLLFUS: BILL; SELIGSOHN).

Recapitulation and Remarks.

§ 239.

The non-volatile alkaloids of the second group are altered or precipitated by various other reagents besides those mentioned above; the reactions are, however, not adapted to effect their individual detection and separation. Thus, for instance, bichloride of platinum produces in solutions of the salts of the three alkaloids belonging to this group a yellowish-white precipitate, chloride of mercury a white precipitate, tincture of galls a yellowish-white flocculent precipitate, solution of iodine in iodide of potassium a reddish-brown, phospho-molybdic acid a yellow precipitate, &c.

Narcotina and quina being soluble in ether, whilst cinchonia is insoluble in that menstruum, the two former alkaloids may be most readily separated by this means from the latter. For this purpose

the analyst need simply mix the aqueous solution of the three alkaloids with ammonia in excess, then add ether, and separate the solution of quina and narcotina from the undissolved cinchonia. If the ethereal solution is now evaporated, the residue dissolved in hydrochloric acid and a sufficient amount of water to make the dilution as 1 : 200, and bicarbonate of soda is then added, the narcotina precipitates, whilst the quina remains in solution. By evaporating the solution, and treating the residue with water, the quina is obtained in the free state.*

THIRD GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSA FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO A PERCEPTIBLE EXTENT IN AN EXCESS OF THE PRECIPITANT; BUT ARE NOT PRECIPITATED FROM (even somewhat concentrated) ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALIES: Strychnia, Brucia, Veratria.

a. STRYCHNIA, or STRYCHNINE ($C_{42}\,H_{22}\,N_2\,O_4 = \overset{+}{Sr}$)

§ 240.

1. Strychnia appears either in the form of white brilliant rhombic prisms, or, when produced by precipitation or rapid evaporation, as a white powder. It has an exceedingly bitter taste. It is nearly insoluble in cold, and barely soluble in hot water. It is almost insoluble in absolute alcohol and ether, and only sparingly soluble in dilute spirit of wine. It dissolves freely in amyl-alcohol, more especially with the aid of heat. It does not fuse when heated. It is exceedingly poisonous.

2. Strychnia neutralizes acids completely. The salts of strychnia are, for the most part, crystallizable; they are soluble in water. All the salts of strychnia have an intolerably bitter taste and are exceedingly poisonous.

3. *Potassa* and *carbonate of soda* produce in solutions of salts of strychnia white precipitates of STRYCHNIA, which are insoluble in an excess of the precipitants. Viewed under a microscope magni-

* The reaction with ammonia and ether, though well adapted to effect the separation of quina from cinchonine, fails to effect the separation of the former vegeto-alkali from the other bases found in bark, which are not as yet officinal, viz., *α* quinidine, *β* quinidine, *γ* quinidine, and cinchonidine; since, as G. KERNER (Zeitschrift f. Analyt. Chem., 1, 150) has shown, several of these other vegeto-alkalics are pretty freely soluble in ether. In fact, no qualitative reaction will enable the analyst to fully effect this purpose; but it may be accomplished by means of a simple volumetrical method, based upon the circumstance that the quina thrown down by ammonia from a solution of the sulphate, requires less ammonia to redissolve it than all the other vegeto-alkalies of the bark. For further particulars I refer to KERNER's paper on the subject.

fying one hundred times the precipitate appears as an aggregate of small crystalline needles. From dilute solutions the strychnia separates only after the lapse of some time, in the form of crystalline needles, which are distinctly visible even to the naked eye.

4. *Ammonia* produces the same precipitate as potassa. The precipitate redissolves in an excess of ammonia; but after a short time—or if the solution is highly dilute, after a more considerable lapse of time—the strychnia crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. *Bicarbonate of soda* produces in neutral solutions of salts of strychnia a precipitate of strychnia, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (so as to leave the fluid still alkaline), the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to an acid solution of strychnia causes no precipitation, and it is only after the lapse of twenty-four hours, or even a longer period, that strychnia crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnia, supersaturated with bicarbonate of soda, is boiled for some time, a precipitate forms at once; from dilute solutions this precipitate separates only after concentration.

6. *Sulphocyanide of potassium* produces in concentrated solutions of salts of strychnia immediately, in dilute solutions after the lapse of some time, a white crystalline precipitate, which appears under the microscope as an aggregate of flat needles, truncated or pointed at an acute angle, and is but little soluble in an excess of the precipitant.

7. *Chloride of mercury* produces in solutions of salts of strychnia a white precipitate, which changes after some time to crystalline needles, aggregated into stars, and distinctly visible through a lens. Upon heating the fluid these crystals redissolve, and upon subsequent cooling of the solution the double compound recrystallizes in larger needles.

8. If a few drops of pure *concentrated sulphuric acid* are added to a little strychnia in a porcelain dish, solution ensues, without coloration of the fluid. If small quantities of oxidizing agents (chromate of potassa, permanganate of potassa, ferricyanide of potassium, peroxide of lead, binoxide of manganese) are now added —best in the solid form, as dilution is prejudicial to the reaction— the fluid acquires a magnificent blue-violet color, which, after some time, changes to wine-red, then to reddish-yellow. With chromate of potassa and permanganate of potassa the reaction is immediate; on inclining the dish, blue violet streaks are seen to flow from the salt fragment, and by pushing the latter about, the coloration is

soon imparted to the entire fluid. With ferricyanide of potassium the reaction is less rapid; but it is slowest with peroxides. The more speedy the manifestation of the reaction the more rapid is also the change of color from one tint to another. I prefer chromate of potassa, recommended by OTTO, or permanganate of potassa, recommended by GUY, as the most sensitive, to all other oxidizing agents. JORDAN succeeded, with chromate of potassa, in distinctly showing the presence of $\frac{1}{70,000}$th grain of strychnia. J. ERDMANN prefers binoxide of manganese in lentil-sized fragments. Metallic chlorides and considerable quantities of nitrates, also large quantities of organic substances, prevent the manifestation of the reaction or impair its delicacy. It is therefore always advisable to free the strychnia first, as far as practicable, from all foreign matters before proceeding to try this reaction. If the solution colored red (by binoxide of manganese) is mixed with from 4 to 6 times its volume of water, and ammonia is then added until the reaction is *nearly* neutral, the fluid shows a magnificent violet-purple tint; upon addition of more ammonia the color becomes yellowish-green to yellow (J. ERDMANN). I have found, however, that this reaction is seen only where larger, though still very minute, quantities of strychnia are present.

9. Strong *chlorine water* produces in solutions of salts of strychnia a white precipitate, which dissolves in ammonia to a colorless fluid.

10. *Concentrated nitric acid* dissolves strychnia and its salts to a colorless fluid, which turns yellow upon the application of heat.

b. BRUCIA, or BRUCINE ($C_{46}H_{26}N_2O_8 = \overset{+}{Br}$).

§ 241.

1. Crystallized brucia ($\overset{+}{Br}$ + 8 aq.) appears either in the form of transparent right rhombic prisms, or in that of crystalline needles aggregated into stars, or as a white powder composed of minute crystalline scales. Brucia is difficultly soluble in cold, but somewhat more readily in hot water. It dissolves freely in alcohol, both in absolute and dilute, also in cold, but more readily still in hot, amyl-alcohol; but it is almost insoluble in ether. Its taste is intensely bitter. When heated, it fuses with loss of its water of crystallization.

2. Brucia neutralizes acids completely. The salts of brucia are readily soluble in water, and of an intensely bitter taste. Most of them are crystallizable.

3. *Potassa* and *carbonate of soda* throw down from solutions of salts of brucia a white precipitate of brucia, which is insoluble in an excess of the precipitant. Viewed under the microscope, im-

mediately after precipitation, it appears to consist of very minute grains; but upon further inspection, these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves without exception into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. *Ammonia* produces in solutions of salts of brucia a whitish precipitate, which appears at first like a number of minute drops of oil, but changes subsequently—with absorption of water—to small needles. The precipitate redissolves, immediately after separation, very readily in an excess of the precipitant; but after a very short time—or, in dilute solutions, after a more considerable lapse of time—the brucia, combined with crystallization water, crystallizes from the ammoniacal fluid in small concentrically grouped needles, which addition of ammonia fails to redissolve.

5. *Bicarbonate of soda* produces in neutral solutions of salts of brucia a precipitate of brucia, combined with crystallization water; this precipitate separates after the lapse of a short time, in form of concentrically aggregated needles of silky lustre, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnia). Bicarbonate of soda fails to precipitate acid solutions of salts of brucia; and it is only after the lapse of a considerable time, and with the escape of the carbonic acid, that the alkaloid separates from the fluid in regular and comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucia and its salts to intensely red fluids, which subsequently acquire a yellowish-red tint, and turn yellow upon application of heat. Upon addition of protochloride of tin or sulphide of ammonium to the heated fluid, no matter whether concentrated or after dilution with water, the faint yellow color changes to a most intense violet.

7. If a little brucia is treated with from 4 to 6 drops of pure *concentrated sulphuric acid*, a solution of a faint rose color is obtained, which afterwards turns yellow. If from 8 to 20 drops of sulphuric acid mixed with some *nitric acid* (p. 394) are added, the fluid transiently acquires a red, afterwards a yellow color. Addition of binoxide of manganese transiently imparts a red, then a gamboge tint to the fluid. If the fluid is then, with proper cooling, diluted with 4 parts of water, *ammonia* added to nearly neutral reaction, or even to alkaline reaction, the solution acquires a gold-yellow color (J. ERDMANN).

8. Addition of *chlorine water* to the solution of a salt of brucia imparts to the fluid a fine bright red tint; if ammonia is then added, the red color changes to yellowish-brown.

9. *Sulphocyanide of potassium* produces in concentrated solutions of salts of brucia immediately, in dilute solutions after some

time, a granular crystalline precipitate, which, when viewed under the microscope, appears composed of variously aggregated polyhedral crystalline grains. Friction applied to the sides of the vessel promotes the separation of the precipitate.

10. *Chloride of mercury* also produces a white granular precipitate, which, when viewed under the microscope, appears composed of small roundish crystalline grains.

c. Veratria, or Veratrine ($C_{64}H_{88}N_2O_{16}$) $\dot{V}e$.

§ 242.

1. Veratria appears in the form of small prismatic crystals, which acquire a porcelain-like look in the air, or as a white or yellowish-white powder of acrid and burning, but not bitter taste; it is exceedingly poisonous. Veratria acts with great energy upon the membranes of the nose; even the most minute quantity of the powder excites the most violent sneezing. It is insoluble in water; in alcohol it dissolves readily, but more sparingly in ether. At 239° Fah. it fuses like wax, and solidifies upon cooling to a transparent yellow mass.

2. Veratria neutralizes acids completely. Some salts of veratria are crystallizable, others dry up to a gummy mass. They are soluble in water, and have an acrid and burning taste.

3. *Potassa*, *ammonia*, and the *mono-carbonates of the alkalies* produce in solutions of salts of veratria a flocculent white precipitate, which, viewed under the microscope, immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals are observed, instead of the original coagulated flakes. The precipitate does not redissolve in an excess of potassa or of carbonate of potassa. It is slightly soluble in ammonia in the cold, but the dissolved portion separates again upon application of heat.

4. With *bicarbonate of soda* and *bicarbonate of potassa* the salts of veratria comport themselves like those of strychnia and brucia. However, the veratria separates readily upon boiling, even from dilute solutions.

5. If veratria is acted upon by *concentrated nitric acid*, it agglutinates into small resinous lumps, which afterwards dissolve slowly in the acid. If the veratria is pure the solution is colorless.

6. If veratria is treated with *concentrated sulphuric acid*, it also agglutinates at first into small resinous lumps; but these dissolve with great readiness to a faint yellow fluid, the color of which gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red. The color per

sists 2 or 3 hours, then disappears gradually. Addition of sulphuric acid, containing nitric acid, or of binoxide of manganese causes no great change of color. If the fluid is then diluted with water, and ammonia added until the reaction is nearly neutral, a yellowish solution is obtained, in which ammonia added in excess produces a greenish light-brown precipitate (J. ERDMANN).

7. *Sulphocyanide of potassium* produces only in concentrated solutions of salts of veratria flocculent-gelatinous precipitates.

8. Addition of *chlorine-water* to the solution of a salt of veratria imparts to the fluid a yellowish tint, which, upon addition of ammonia, changes to a faint brownish color. In concentrated solutions chlorine produces a white precipitate.

[9. *Cold concentrated hydrochloric acid* dissolves veratria to a colorless solution, which, on prolonged boiling, assumes a red color that finally becomes very intense and resembles that of permanganate of potassa. The colored liquid remains unaltered for a long time. This reaction is very sensitive. TRAPP.*

Recapitulation and remarks.

§ 243.

The alkaloids of the third group also are precipitated by many other reagents besides those above mentioned, as, for instance, by tincture of galls, bichloride of platinum, solution of iodine in iodide of potassium, phosphomolybdic acid, &c. But as these reactions are common to all, they are of little importance in an analytical point of view.†

Strychnia may be separated from brucia and veratria by means of absolute alcohol, since it is insoluble in that menstruum, whilst the two latter alkaloids readily dissolve in it. The identity of strychnia is best established by the reaction with sulphuric acid and the above-mentioned oxidizing agents;‡ also by the form of its crystals—when thrown down by alkalies—viewed under the microscope; and lastly, by the form of the precipitate which sulphocyanide of potassium and chloride of mercury produce in

* *Polytechnisches Notizblatt*, 1863, 96.

† If the precipitate produced in the solution of a salt of strychnia by iodide of potassium containing iodine, is dissolved in spirit of wine mixed with some sulphuric acid and the solution is evaporated, strongly polarizing prismatic crystals of sulphate of iodide of strychnia are obtained. DE VRIJ and VAN DER BURG (Jahresber v. LIEBIG, and KOPP, 1857, 602). Whether this reaction is characteristic for strychnia, can be known only after the optical properties of analogous compounds of the other alkaloids shall have been studied.

‡ The only substance which shows somewhat analogous reactions in this respect, is aniline. A. GUY has, however, called attention to the fact that aniline, treated with sulphuric acid and oxidizing agents, acquires a pale green color at first, which gradually deepens, and only then changes to a magnificent blue, which, after persisting some time turns finally black.

solutions of its salts. Brucia and veratria are not readily separated from one another, but may be detected in presence of each other. The identity of brucia is best established by the reactions with nitric acid and protochloride of tin or sulphide of ammonium, or by the form of the crystalline precipitate which ammonia produces in solutions of salts of brucia. Veratria is sufficiently distinguished from brucia and the other alkaloids which we have treated of, by its characteristic deportment at a gentle heat, and also by the form of the precipitate which alkalies produce in solutions of its salts. To distinguish veratria in presence of brucia, the reaction with concentrated sulphuric acid is selected.

To these alkaloids I will add *salicine*, though this substance does not properly belong to the same class of chemical compounds.

§ 244.

Salicine ($C_{26}H_{18}O_{14}$).

1. Salicine appears either in the form of white crystalline needles and scales of silky lustre, or, where the crystals are very small, as a powder of silky lustre. It has a bitter taste, is readily soluble in water and in alcohol, but insoluble in ether.

2. No reagent precipitates salicine as such.

3. If salicine is treated with *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving in the acid; the color of the sulphuric acid is at first unaltered.

4. If an aqueous solution of salicine is mixed with *hydrochloric acid* or *dilute sulphuric acid*, and the mixture boiled for a short time, the fluid suddenly becomes turbid, and deposits a fine granular crystalline precipitate (saliretine).

Systematic Course for the Detection of the Alkaloids treated of in the preceding Paragraphs, and of Salicine.

The analytical course which I am now about to describe is based upon the supposition that the analyst has to examine a concentrated aqueous solution—effected by the agency of an acid—of one or several of the non-volatile alkaloids, which solution is free from any admixture of substances that might tend to obscure or modify the reactions. For the modifications which the presence of coloring or extractive matters, &c., requires, I refer to § 247.

I. Detection of the Alkaloids, and of Salicine, in Solutions supposed to contain only one of these Substances.*

§ 245.

1. Add dilute solution of potassa or soda, drop by drop, to a

* Where the detection of one of the five more frequently occurring poisonous alkaloids alone is the object, the following simple method devised by J. Erdmann, will fully answer the purpose:

portion of the aqueous solution until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. NO PRECIPITATE IS FORMED; this proves the total absence of the alkaloids, and indicates the presence of SALICINE. To set all doubt at rest, test the original substance with concentrated sulphuric acid, and also with hydrochloric acid. Compare § 244.

b. A PRECIPITATE IS FORMED. Add solution of potassa or soda, drop by drop, until the fluid manifests a strongly alkaline reaction.

a. The precipitate redissolves: MORPHIA. To arrive at a positive conclusion on this point, test another portion of the solution with iodic acid (§ 235, 9), and a portion of the original substance with sulphuric acid, &c., (§ 235, 7).

In this method, which is more especially applicable in cases where the disposable quantity of substance is very small, the alkaloids are supposed to be present in the pure state and in the solid form.

1. Treat the substance under examination with from 4 to 6 drops of pure concentrated sulphuric acid.

Yellow color, speedily changing to red: VERATRIA.

Rose color, changing afterwards to BRUCIA.

The other alkaloids, if pure, impart no color to the sulphuric acid.

2. No matter whether there is color or not; add to the fluid obtained in 1, from 8 to 20 drops of concentrated sulphuric acid mixed with nitric acid (see foot-note to § 235, 7), then two or three drops of water. After a quarter or half-hour the fluid shows:

a. a violet-red color: MORPHIA;

b. an onion-red color: NARCOTINA;

c. a transient red tint, changing to yellow: BRUCIA;

d. the red color of the sulphuric acid solution of VERATRIA is not materially altered;

e. with STRYCHNIA no coloration is observed.

3. Put into the fluid obtained in 2, no matter whether colored or not, from 4 to 6 clean fragments of binoxide of manganese, of the size of a lentil. After an hour the fluid shows;

a. a mahogany-brown color: MORPHIA;

b. a yellowish-red to blood-red color: NARCOTINA;

c. a transient purple-violet tint, changing to deep onion-red: STRYCHNIA;

d. a transient red tint, changing to gamboge-yellow: BRUCIA;

e. a dark dirty cherry-red color: VERATRIA;

4. Pour the colored fluid obtained in 3, into a test tube containing 4 times the volume of water, and add ammonia until the neutralization point is *almost* attained. Heat must be as much as possible avoided in these operations.

a. dirty-yellow color, changing to brownish-red upon supersaturation with ammonia, without immediate deposition of a notable precipitate: MORPHIA;

b. reddish coloration, more or less intense according to the degree of dilution; upon supersaturation with ammonia, copious dark-brown precipitate: NARCOTINA;

c. violet-purple colored solution, becoming yellowish-green to yellow upon addition of ammonia in excess: STRYCHNIA;

d. gold-yellow solution, not materially changed by excess of ammonia: BRUCIA;

e. faint brownish solution, turning yellowish upon further addition of ammonia, and depositing a greenish light-brown precipitate: VERATRIA.

β. The precipitate remains undissolved: Presence of an alkaloid of the second or third group. Pass on to 2.

2. Add to a second portion of the original solution two or three drops of dilute sulphuric acid, then a saturated solution of bicarbonate of soda until the acid reaction is just neutralized; vigorously rub the inside of the vessel, and allow the mixture to stand for half an hour.

a. NO PRECIPITATE IS PRODUCED: Absence of narcotina and cinchonia. Pass on to 3.

b. A PRECIPITATE IS FORMED: Narcotina, cinchonia, and perhaps also quina, as the precipitation of the latter substance by bicarbonate of soda depends entirely upon the degree of dilution of the fluid. Add to a portion of the original solution ammonia in excess, then a sufficient quantity of ether, and shake the mixture.

α. The precipitate which forms at first upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers: narcotina or quina. To distinguish between the two, test a fresh portion of the original solution with chlorine water and ammonia. If the solution turns green, QUINA, if yellowish-red, NARCOTINE is present. The reaction with a mixture of sulphuric acid and nitric acid (§ 236, 5) is resorted to as a conclusive test.

β. The precipitate which forms upon the addition of ammonia does not redissolve in the ether—CINCHONIA. The deportment of cinchonia at a high temperature (§ 238, 3), or the reaction with ferricyanide of potassium (§ 238, 8), may serve as a conclusive test.

3. Put a portion of the original substance, or of the residue remaining upon the evaporation of the solution, on a watch-glass, and treat with concentrated sulphuric acid.

a. A rose-coloured solution is obtained, which becomes intensely red upon addition of nitric acid: BRUCIA. The reaction with nitric acid and protochloride of tin is resorted to as a conclusive test (§ 241, 6).

b. A yellow solution is obtained, the color of which gradually changes to yellowish-red, then to blood-red, and turns finally crimson: VERATRIA.

c. A colorless fluid is obtained, which remains colorless after standing for some time.

Add to the fluid a fragment of chromate of potassa; if this imparts to it a deep blue color, STRYCHNIA is present; if it leaves the fluid unaltered, QUINA is present. The reaction with chlorine water and ammonia is resorted to as a conclusive test.

II. Detection of the Alkaloids, and of Salicine, in Solutions supposed to contain several or all of these Substances.

§ 246.

1. Add to a portion of the aqueous solution dilute solution of potassa or soda, drop by drop, until the fluid acquires a scarcely perceptible alkaline reaction; stir, and let the fluid stand for some time.

a. No precipitate is formed; this proves the total absence of the alkaloids, and indicates the presence of salicine. To remove all doubt on the point, test the original substance with concentrated sulphuric acid, and with hydrochloric acid. Compare § 245, 1, *a.*

b. A precipitate is formed: add solution of potassa or soda, drop by drop, until the fluid manifests a strongly alkaline reaction.

α. The precipitate redissolves. Absence of the alkaloids of the second and third groups. Presence of morphia is indicated. The reactions with iodic acid (§ 235, 9), and with sulphuric acid, &c. (§ 235, 7), are resorted to as conclusive tests. Examination for salicine, see 4.

β. The precipitate does not redissolve, or at least not completely. Filter, and treat the precipitate as directed in 2. Saturate the filtrate with carbonic acid, or mix it with bicarbonate of soda or bicarbonate of potassa, and boil nearly to dryness. Treat the residue with water; if it dissolves completely, this is a sign that no morphia is present; but if there is an insoluble residue left, this indicates the presence of morphia. The reactions with iodic acid (§ 235, 9), and with sulphuric acid, &c. (§ 235, 7), are resorted to as conclusive tests.

2. Wash the filtered precipitate of 1, *b*, *β*, with cold water, dissolve in a slight excess of dilute sulphuric acid, and add solution of bicarbonate of soda to the fluid until the acid reaction is neutralized; stir the mixture, vigorously rubbing the sides of the vessel, and allow the fluid to stand for an hour.

a. No Precipitate is formed. Absence of narcotina and cinchonia. Boil the solution nearly to dryness, and treat the residue with cold water. If it dissolves completely, pass on to 4; but if an insoluble residue is left, examine this for quina—of which a minute quantity might be present—and for strychnia, brucia, and veratria, according to the directions of 3.

b. A precipitate is formed. This may contain narcotina, cinchonia, and also quina, compare § 245, 2, *b.* Filter, and treat the filtrate as directed § 246, 2, *a.* Wash the precipitate with cold water, dissolve in a little hydrochloric acid, add ammonia in excess, then a sufficient quantity of ether.

α. The precipitate which forms at first upon the addition of

the ammonia redissolves completely in the ether, and the clear fluid presents two distinct layers. Absence of cinchonia; presence of quina or narcotina. Evaporate the ethereal solution, dissolve the residue in a little hydrochloric acid and a sufficient amount of water to make the dilution at least as 1 : 200; add bicarbonate of soda to neutralization, and allow the fluid to stand for some time. The formation of a precipitate indicates the presence of NARCOTINA. Filter, and test the precipitate with chlorine water and ammonia, and with a mixture of sulphuric acid and nitric acid (§ 236). Evaporate the filtrate, or the fluid if no precipitate has formed, to dryness, and treat the residue with water. If part of it remains undissolved, wash this, dissolve in hydrochloric acid, and add chlorine water and ammonia. Green color: QUINA.

β. The precipitate produced by the ammonia does not redissolve in the ether, or at least not completely: CINCHONIA. Quina or narcotina may also be present. Filter, and examine the filtrate for quina and narcotina as in *α*. The precipitate consists of cinchonia, and may be further examined according to § 238, 3, or 8.

3. Wash the insoluble residue of § 246, 2, *α*, with water, dry on the water-bath, and digest with absolute alcohol.

α. IT DISSOLVES COMPLETELY: absence of strychnia; presence of (quina) brucia or veratria. Evaporate the alcoholic solution on the water-bath to dryness, and, if quina has already been detected, divide the residue into two portions, and test one part for BRUCIA, with nitric acid and protochloride of tin (§ 241, 6), the other for VERATRIA, by means of concentrated sulphuric acid (§ 242, 6); but if no quina has as yet been detected, divide the residue into three portions, *a*, *b*, and *c*; examine *a* and *b* for BRUCIA and VERATRIA, in the manner just stated, and *c* for quina, with chlorine-water and ammonia. However, if brucia is present, dissolve *c* in hydrochloric acid, add ammonia and ether, let the mixture stand for some time, evaporate the ethereal solution, and examine the residue for quina.

b. It does not dissolve, or at least not completely: presence of STRYCHNIA; perhaps also of (quina) brucia and veratria. Filter, and examine the filtrate for (QUINA) BRUCIA and VERATRIA as directed § 246, 3, *α*. The identity of the precipitate with strychnia is demonstrated by the reaction with sulphuric acid and chromate of potassa (§ 240, 8).

4. Mix a portion of the original solution with hydrochloric acid, and boil the mixture for some time. The formation of a precipitate indicates the presence of SALICINE. To set all doubt on this point at rest, test the original substance with concentrated sulphuric acid (§ 244, 3).

III. Detection of the Alkaloids, in presence of coloring and extractive Vegetable or Animal Matters.

§ 247.

The presence of mucilaginous, extractive, and coloring matters renders the detection of the alkaloids a task of considerable difficulty. These matters obscure the reactions so much that we are even unable to determine by a preliminary experiment, whether the substance under examination contains one of the alkaloids we have treated of in the foregoing paragraphs, or not. I will now give several methods by means of which the separation of the alkaloids from such extraneous matters may be effected, and their detection made practicable. Which of these methods to select will, of course, always depend upon the particular circumstances of the case.

1. Stas's Method for effecting the Detection of Poisonous Alkaloids.*

This method is based, *a*, upon the solubility of the acid salts of the alkaloids in water and in spirit of wine; *b*, upon the fact that the alkaloids, even those sparingly soluble in ether, will pass into the ethereal solution upon mixing the aqueous solution of any of their salts with a fixed alkali or with the carbonate of a fixed alkali in excess, and shaking the mixture repeatedly with ether;—lastly, *c*, the removal from the alkaloids of other matters soluble in ether, is based upon the insolubility of the salts of the alkaloids in ether, owing to which an aqueous solution of the acid sulphate of the alkaloid can be obtained, by shaking the ethereal solution of the pure alkaloid with dilute sulphuric acid. I will give here, first the original method of Stas, then, in 2, Otto's modifications of that method.

a. If you have to look for the suspected organic bases in the contents of the stomach or intestines, or in articles of food, or in pappy matters in general, heat the suspected substance with double its weight of strong alcohol, acidified with from 0·5 grm. to 2 grm. of tartaric acid or oxalic acid, to from 158° F. to 167° F. When quite cold, filter, and wash the undissolved part with strong alcohol, adding the washings to the filtrate.

If you have to deal with the heart, liver, lungs, or similar organs, cut them into fine shreds, moisten with the acidified alcohol, press, and repeat the same operation, until the soluble parts are completely extracted; collect the fluids obtained, and filter.

b. Concentrate the alcoholic fluid at a temperature not exceeding 95° F., and, if no insoluble matter separates, continue to evaporate

* "Bulletin de l'Académie de Médecine de Belgique," IX. 304. "Jahrb. f. prakt Pharm.," XXIV. 313. "Jahresbericht" von Liebig und Kopp, 1851, p. 640.

nearly to dryness. Conduct this process either under a bell-glass over sulphuric acid, with or without rarefaction of the air, or in a tubulated retort, through which a current of air is passed. If fatty or other insoluble matters separate in the process of concentration, pass the concentrated fluid through a moistened filter, and evaporate the filtrate nearly to dryness, conducting the process, as above, either under a bell-glass or in a retort.

c. Digest the residue with cold absolute alcohol, filter, wash the insoluble residue thoroughly with alcohol, and let the alcoholic solution evaporate in the air or in vacuo; dissolve the acid residue in a little water, and add bicarbonate of soda as long as effervescence ensues.

d. Add to the mixture four or five times its volume of pure ether, free from oil of wine, and shake; then allow it to stand at rest, and let a little of the supernatant ether evaporate spontaneously on a watch-glass. If this leaves oily streaks upon the glass, which gradually collect into a drop, and emit, upon the application of a gentle heat a disagreeable, pungent, and stifling odor, there is reason to infer the presence of a liquid volatile base; whilst a solid residue or a turbid fluid, with solid particles suspended in it, indicates a non-volatile, solid base. In the latter case the base may emit a disagreeable animal smell, but not a pungent odor, as is the case with volatile bases. The blue color of reddened litmus-paper is permanently restored. If no residue is left, add to the fluid some solution of soda or potassa, and shake with repeatedly renewed ether, which will now dissolve the base. It follows from the assumption that the bases present will pass into the ethereal solution, that Stas's method is principally calculated for the detection of the poisonous alkaloids which are soluble in ether, though some of them only sparingly. The following are the vegeto-alkalies which Stas enumerates as discoverable by his method: Conia, Nicotina, Aniline, Picoline, Petinine, Morphia, Codeia, Brucia, Strychnia, Veratria, Colchicia, Delphia, Emetine, Solania, Aconitina, Atropia, and Hyoscyamia.

α. There is reason to infer the presence of a volatile base.

Add to the contents of the vessel from which you have taken the small portion of ether for evaporation on the watch-glass, one or two cubic centimetres of strong solution of potassa or soda, shake the mixture, let it stand at rest, pour the supernatant fluid into a flask, and treat the residue again three or four times with ether, until the last portion poured off leaves no longer a residue upon evaporation. Mix the ethereal fluid now with some dilute sulphuric acid (1 part of acid to 5 parts of water) until the well-shaken fluid manifests acid reaction; allow the mixture to stand at rest, decant the supernatant ether from the acid aqueous fluid, and treat the latter once more with ether in the same way.

aa. Mix the residual acid solution (which may contain sulphates of ammonia, nicotina, aniline, picoline, and petinine—indeed which must contain these bases, if they are present in the examined substance, since their compounds with sulphuric acid are quite insoluble in ether; and in which, if conia is present, the greater part of the latter alkaloid is also found) with concentrated solution of soda or potassa in excess, and treat with ether, which will again dissolve the liberated bases; decant the ether, and leave it to spontaneous evaporation, at the lowest possible temperature; place the dish with the residue in vacuo over sulphuric acid. In this process, the ether and ammonia escape, leaving the volatile organic base in the pure state. The nature of the organic base is then finally ascertained.

bb. The ether decanted from the acid solution contains the animal matters which it has removed from the alkaline fluid. It leaves, therefore, upon spontaneous evaporation, a trifling faint yellow residue of nauseous odor, which contains also some sulphate of conia, if that base was present in the examined matter.

β. There is reason to infer the presence of a solid base.

Add a few drops of alcohol to the ethereal solution obtained by treating with ether the previously acid residue mixed either simply with bicarbonate of soda, or first with that reagent, then with solution of soda or potassa (see *c* and *d*), and leave the mixture to spontaneous evaporation. If this fails to give the base in a distinctly crystalline form and sufficiently pure, add a few drops of water slightly acidified with sulphuric acid, which will usually serve to separate the mass into a fatty portion, adhering to the dish, and an acid aqueous solution, which contains the base as an acid sulphate. Decant or filter, wash with a little slightly acidified water, and evaporate the solution to a considerable extent, under a bell-glass over sulphuric acid. Mix the residue with a highly concentrated solution of pure carbonate of potassa, treat the mixture with absolute alcohol, decant, and let the alcoholic fluid evaporate, which will generally leave the base in a state of perfect purity, or nearly so.

2. Otto's Modifications of Stas's Method.*

a. In the method just described, the morphia which may be present will only pass into the ethereal solution if the solution obtained in 1, *c*, is shaken with ether immediately after the addition of the bicarbonate of soda, and the ether then quickly decanted. But if the operation of shaking with ether is delayed, so as to af-

* Annal. d. Chem. u. Pharm., 100, 44.

ford the morphia time to crystallize, the crystals will deposit, being almost absolutely insoluble in ether (P. Pöllnitz); and if the ethereal solution is allowed to stand some time, the dissolved morphia will separate in small crystals, on the sides of the vessel.—As it is therefore, under the circumstances stated, always likely to happen that the morphia may remain, wholly or in part, undissolved by the ether, it is of the highest importance never to neglect mixing the alkaline fluid obtained in 1, *d*—after repeated extraction with ether, and subsequent addition of some solution of soda, to dissolve the morphia, which may have separated, and after evaporating the ether still present—with a concentrated solution of chloride of ammonium, and letting the mixture stand exposed to the open air, to allow the morphia to crystallize.

b. Instead of the process described in 1, *β*, to effect the detection of non-volatile alkaloids, Otto recommends the following method, which is in principle the same as that recommended by Stas for the detection of the volatile bases.

Let the ethereal solution evaporate, dissolve the residuary impure alkaloid in a little water mixed with sulphuric acid, and shake the solution repeatedly with ether, which will remove the foreign organic matters present, and leave the acid vegeto-alkaline sulphate unaffected. Mix now the acid aqueous solution with carbonate of soda in excess, shake repeatedly with ether (to dissolve the liberated alkaloids), and let the ethereal solution evaporate, when the alkaloids held in solution by the ether will be left in a very pure state and, to a great extent, in the crystalline form. This method has stood the test of numerous experiments.

c. But what Otto recommends most, is the treatment with ether of the alkaloid in the form of salt, before its separation, by means of an alkali, and its solution in ether.—If, therefore, you wish to follow this method, shake the acid aqueous fluid of 1, *c*, which contains the alkaloid in combination with tartaric acid or oxalic acid, repeatedly with ether, so long as the ether becomes colored and leaves a residue upon evaporation; then, and not before, add carbonate of soda, dissolve the alkaloid by means of ether, and proceed generally as directed in 1, *d*. Upon evaporating the ether, the alkaloid is now left at once in a very pure state.

3. Method of L. V. Uslar and J. Erdmann.*

This may be considered an improvement upon Stas's method, as regards non-volatile alkaloids, more especially morphia, whilst Stas's method deserves the preference for volatile alkaloids. The new method is the same in principle as that of Stas's, simply substituting amyl-alcohol for ether.

* Annal. d. Chem. u. Pharm., 120, page 121; and 122, page 360.

Mix the matters to be examined with water, if necessary, to the consistence of a thin paste, acidify slightly with hydrochloric acid, digest one or two hours at from 140° to 176° Fah., and pass through a linen cloth moistened with water. Extract the residue with water acidified with hydrochloric acid, add the solution obtained to the first fluid, supersaturate with ammonia, and evaporate to dryness, with addition of pure quartz sand, which will enable you to reduce the residue to powder. Boil the powder repeatedly with amyl-alcohol, to extract the whole of the alkaloid from it. Filter the extracts hot through paper moistened with amyl-alcohol. The filtrate, which is mostly colored yellow, holds, besides the alkaloid, fatty and coloring matters in solution. To remove these latter, transfer the filtrate to a cylindrical vessel, mix it with from ten to twelve times its volume of almost boiling water, acidified with hydrochloric acid, and vigorously shake the mixture for some time. The hydrochlorate of the alkaloid passes into the aqueous solution, whilst the fatty and coloring matters remain dissolved in the amyl-alcohol.* Remove the latter by means of an India-rubber pipette, then shake the acid solution repeatedly with fresh quantities of amyl-alcohol, until all the fatty and coloring matters are completely removed. Concentrate now by evaporation, mix with ammonia in slight excess, add hot amyl-alcohol, and shake vigorously. When the liquid has separated into two distinct layers, draw off, by means of a pipette, the upper layer, which contains the solution of the alkaloid in amyl-alcohol, treat the fluid once more with hot amyl-alcohol, then completely drive off the latter by heating on the water-bath, which will often leave the alkaloid sufficiently pure for examination by the usual reactions. Should it, however, still look yellowish or brownish, dissolve it once more in dilute hydrochloric acid, shake the solution with amyl-alcohol, remove the latter with the pipette, then supersaturate with ammonia, shake again with amyl-alcohol, draw off the latter with the pipette, and evaporate it on the water-bath. It is only in very rare cases that the alkaloid left by this evaporation requires a repetition of this process of purification. The last evaporation of the pure alkaloid is best conducted in a small porcelain crucible, placed obliquely. Before proceeding to the decisive reaction, pour a few drops of concentrated sulphuric acid over the alkaloid, and observe whether it still turns brown on the application of this test; in which case the process of purification must be repeated.—Uslar and Erdmann have detected and isolated by this method very minute traces of

* If less water is used, traces of the hydrochlorate of the alkali are apt to remain in the amyl-alcoholic solution. J. Erdmann recommends always to put aside the first portion of amyl-alcohol, as well as that used to effect the removal of the fatty matters that they may, if necessary, be shaken once more with the stated quantity of acidulated water.

alkaloids, *e.g.*, 5 milligrammes of hydrochlorate of morphia, 1 drop of nicotine, 9 milligrammes of strychnine, mixed with from 2 to 3 pounds of contents of the stomach. In his second paper on the subject ERDMANN calls particular attention to the fact that he succeeded in separating by this method the poisonous alkaloids from quite putrid intestines of poisoned animals, from a fortnight to a month after death. The latter experiments referred to strychnia and morphia. Of course only those portions of the alkaloids can be detected which have not yet suffered decomposition. With regard to morphia, there would seem to exist no doubt but that this alkaloid suffers decomposition in the organism. A rabbit had given it 0.1 grm. of hydrochlorate of morphia, and was killed three and a half hours after: no morphia was found in the urine, brain, and spinal marrow; only very little of it in the blood, a little in the stomach and the small intestines, more in the other intestines.

4. METHODS OF DETECTING STRYCHNIA, BASED UPON THE USE OF CHLOROFORM.*

a. RODGERS AND GIRDWOOD'S METHOD.†

Digest the substance under examination with dilute hydrochloric acid (1 part of acid to 10 parts of water) and filter; evaporate the filtrate on the water-bath to dryness, extract the residue with spirit of wine, evaporate the solution, treat the residue with water, filter, supersaturate the filtrate with ammonia, add ½ oz. (15 grammes) of chloroform, shake, transfer the chloroform to a dish, by means of a pipette, evaporate on the water-bath, moisten the residue with concentrated sulphuric acid, to effect carbonization of foreign organic matters, treat with water, after the lapse of several hours, then filter. Supersaturate the filtrate again with ammonia, and shake it with about 1 drachm (4 grammes) of chloroform. Repeat the same operation until the residue left upon the evaporation of the chloroform is no longer charred by sulphuric acid. Transfer the chloroform solution which leaves a pure residue, no longer affected by sulphuric acid, drop by drop, by means of a capillary tube, to the same spot on a heated porcelain dish, letting it evaporate, then test the residue with sulphuric acid and chromate of potassa. RODGERS and GIRDWOOD succeeded in detecting by this method so small a quantity of strychnia as the $\frac{1}{1,0\,0\,0}$th part of a grain.

* These methods are no doubt useful also for effecting the separation of other alkaloids; however, the deportment of the latter with chloroform has not yet been sufficiently studied.

† LIEBIG and KOPP'S "Jahresbericht," 1857, 603.—Pharm. Journ. Trans., xvi. 497.

b. METHOD RECOMMENDED BY E. PROLLIUS.*

Boil twice with spirit of wine, mixed with some tartaric acid, evaporate at a gentle heat, filter the residuary acid aqueous solution through a moistened filter, add ammonia in slight excess, then from 20 to 25 grains (about 1½ grm.) of chloroform, shake, free the deposited chloroform thoroughly from the ley, by decanting and shaking with water, mix the chloroform so purified with 3 parts of spirit of wine, and let the fluid evaporate. If there is any notable quantity of strychnia present, it is obtained in crystals.

5. METHOD OF EFFECTING THE DETECTION OF STRYCHNIA IN BEER, BY *Graham* AND *A. W. Hofman.*†

This method, which is based on the known fact that a solution of a salt of strychnia, when mixed and shaken with animal charcoal, yields its strychnia to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloids. The process is conducted as follows:—

Shake 2 ounces of animal charcoal in half-a-gallon of the aqueous neutral or feebly acid fluid under examination; let the mixture stand for from 12 to 24 hours, with occasional shaking, filter, wash the charcoal twice with water, then boil for half-an-hour with 8 ounces of spirit of wine of 80–90 per cent., avoiding loss of alcohol by evaporation. Filter the spirit of wine hot from the charcoal, and distil the filtrate; add a few drops of solution of potassa to the residual watery fluid, shake with ether, let the mixture stand at rest, then decant the supernatant ether. The ethereal fluid leaves, upon spontaneous evaporation, the strychnia in a state of sufficient purity to admit of its further examination by reagents (see § 240).

MACADAM‡ employed the same method in his numerous experiments to detect strychnia in the bodies of dead animals. He treated the comminuted matters with a dilute aqueous solution of oxalic acid in the cold, filtered through muslin, washed with water, heated to boiling, filtered still warm, from the coagulated albuminous matters, shook with charcoal, and proceeded in the manner just described. According to his statements, the residue left by the evaporation of the alcoholic solution was generally at once fit to be tested for strychnia. Where it was not so, he treated the residue again with solution of oxalic acid, and repeated the process with animal charcoal.

6. SEPARATION BY DIALYSIS.

The dialytic method devised by GRAHAM, and described in § 227,

* Chem. Centrabl., 1857, 231.

† Chem. Soc. Quart. Journ., v. 173.

‡ Pharm. Journ. Trans., xvi. 120, 160.

may also be advantageously employed to effect the separation of alkaloids from the contents of the stomach, intestines, &c. Acidify with hydrochloric acid, and place the matter in the dialyser. The alkaloids, being crystalline bodies, penetrate the membrane, and are found, for the greater part, after 24 hours, in the outer fluid; from this they may, then, according to circumstances, either be thrown down at once, after concentration by evaporation; or they may be purified by one of the above described methods.

II.

General Plan of the Order and Succession in which Substances should be analyzed for Practice.

§ 248.

It is not a matter of indifference whether the student, in analyzing for the sake of practice, follows no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways, indeed, may lead to the desired end, but one of them will invariably prove the shortest. I will, therefore, here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

Let the student take 100 compounds, systematically arranged (*see below*), and let him analyze these compounds successively in the order in which they are placed. A careful and diligent examination of these will be amply sufficient to impart to him the necessary degree of skill in practical analysis. When analyzing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed for him by a friend who knows their exact composition.

A. *From* 1 *to* 20.

Aqueous solutions of simple salts: *e. g.*, sulphate of soda, nitrate of lime, chloride of copper, &c. These investigations will serve to teach the student the method of analyzing substances soluble in water which contain but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination; but neither the detection of the acid, nor the proof of the absence of all other bases besides the one detected, is required.

B. *From* 21 *to* 50.

SALTS, ETC., CONTAINING ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID (in form of powder: *e. g.*, carbonate of baryta, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, bitartrate of potassa, acetate of copper, sulphate of baryta, chloride of lead, &c. These investigations will serve to teach the student how to make a preliminary examination of a solid substance, by heating in a tube or before the blowpipe; how to convert it into a proper form for analysis, *i. e.*, how to dissolve or decompose it; how to detect *one* metallic oxide, even in substances *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the base and the acid is required, but it is not necessary to prove that no other bodies are present.

C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides from each other. The proof is required that no other bases are present besides those detected. No regard is paid to the acids.

D. *From* 66 *to* 80.

DRY MIXTURES OF EVERY DESCRIPTION. A portion of the salts should be organic, another inorganic; a portion of the compounds soluble in water or hydrochloric acid; another insoluble; *e. g.*, mixtures of chloride of sodium, carbonate of lime, and oxide of copper;—of phosphate of magnesia and ammonia, and arsenious acid; of tartrate of lime, oxalate of lime, and sulphate of baryta;—of phosphate of soda, nitrate of ammonia, and acetate of potassa, &c.

These investigations will serve to teach the student how to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates of the alkaline earths; and they will serve as a general introduction to scientific and practical analysis. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

NATIVE COMPOUNDS, ARTICLES OF COMMERCE, &c. Mineral and other waters, minerals of every description, soils, potash, soda, alloys, colors, &c.

III.

Arrangement of the Results of the Analysis performed for Practice.

§ 249.

The manner in which the results of analytical investigations ought to be arranged is not a matter of indifference. The following examples will serve to illustrate the method which I have found the most suitable in this respect.

Plan of arranging the Results of Experiments, Nos. 1—20.

Colorless fluid of neutral reaction.

H Cl	H_2S	NH_4S	NH O, C O and N H Cl
no precipitate, consequently no Ag O, Hg_2O	*no precipitate,* no Pb O, „ Hg O, „ Cu O, „ Bi O_3, „ Cd O	no Fe O, „ Mn O, „ Ni O, „ Co O, „ Zn O	*a white precipitate,* consequently either Ba O, Sr O, or Ca O, no precipitate by solution of sulphate of lime, consequently LIME.
	„ $As O_3$, „ $As O_5$, „ $Sb O_3$, „ $Sn O_2$, „ Sn O, „ Au O^1, „ $Pt O_2$	„ Al_2O_3, „ Cr_2O_3	Confirmation by means of $\overline{O}$
	„ Fe_2O_3		

Plan of arranging the Results of Experiments, Nos. 21–50.

White powder, fusing in the water of crystallization upon application of heat, then remaining unaltered—soluble in water—reaction neutral.

HCl	H S	NH_4S	NH O, C O, and N H Cl	2 Na O, H O, PO_5 and NH_4O
no precipitate.	*no precipitate.*	*no precipitate.*	*no precipitate.*	*a white precipitate,* consequently MAGNESIA.

The detected base being Mg O, and the analyzed substance being soluble in water, the acid can only be Cl, I, Br, SO, NO, $\overline{A}$, &c. The preliminary examination has proved the absence of the organic acids, and of nitric acid.

Ba Cl produces a white precipitate which H Cl fails to dissolve; consequently SULPHURIC ACID.

Plan of arranging the Results of Experiments, nos. 51—100.

A *white powder, acquiring a permanent yellow tint upon application of heat, without forming a sublimate, and without emitting visible fumes marked by acid or alkaline reaction. Before the blowpipe, a ductile metallic globule, and yellow incrustation, with white border upon cooling. Insoluble in water, effervescing with hydrochloric acid, incompletely soluble in that acid, readily soluble in nitric acid to a colorless fluid.*

H Cl	H S	N H_3, S	N H_4 O, CO_2	No fixed residue upon evaporation.	Hydrate of lime has failed to evolve ammonia.
White precipitate, insoluble in an excess of the precipitant, unaltered by ammonia; quite soluble in hot water; SO_3 producing a white precipitate in the solution: LEAD.	Black precipitate, insoluble in sulphide of ammonium, readily soluble in nitric acid. SO_3 produces a white precipitate: LEAD. Examination for Cu, Bi, and Cd: results negative.	White precipitate; ammonia, applied by itself, produces no precipitate; solution of precipitate in hydrochloric acid remains clear upon addition of soda in excess. N H_3, Cl: no precipitate. H S: white precipitate: ZINC.	White precipitate; upon dissolving this in hydrochloric acid, and adding solution of sulphate of lime to the fluid, a white precipitate forms after some time: STRONTIA. Precipitation with sulphate of potassa, filtrate tested for lime with $\bar{O}$: results negative.		

Of the acids CARBONIC ACID has already been found. Of the remaining acids the following cannot be present:

The preliminary examination has proved the absence of organic acids with nitric acid.

Cl O_3 cannot be present, because the analyzed substance is insoluble in water.

S and S O_2 not, because the analyzed substance is readily soluble in nitric acid.

Cr O_3 not, as the nitric acid solution is colorless.

P O_5, Si O_2, H F, and $\bar{O}$ not, because the solution filtered from the sulphide of lead was not precipitated by simple addition of ammonia.

B O_3 might be present in trifling quantity; the examination for it gave a negative result.

Cl, I, Br might be present in the form of basic compounds of lead. However, nitrate of silver has produced no precipitate in the nitric acid solution: accordingly, they cannot be present.

The analyzed compound contains, therefore { bases: oxide of lead, oxide of zinc, strontia. / acids: carbonic acid.

IV.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES TREATED OF IN THE PRESENT WORK,

ARRANGED

WITH ESPECIAL REGARD TO THE CLASS TO WHICH THEY RESPECTIVELY BELONG ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, IN NITRIC ACID, OR IN NITROHYDROCHLORIC ACID.

---

§ 250.

PRELIMINARY REMARKS.

The class to which the several compounds respectively belong according to their solubility in water or acids (see § 182), is expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid; 3 or III a substance insoluble in water, in hydrochloric acid, and in nitric acid. For those substances which stand as it were on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance sparingly soluble in water, but soluble in hydrochloric acid or nitric acid; 1—3 a body sparingly soluble in water, and of which the solubility is not notably increased by the addition of acids; and 2—3 a substance insoluble in water, and sparingly soluble in acids. Wherever the deportment of a substance with hydrochloric acid differs materially from that which it exhibits with nitric acid, this is stated in the notes.

The Roman figures denote officinal and more commonly occurring compounds.

The haloid salts and sulphur compounds are placed in the col-

umns of the corresponding oxides. The salts given are, as a general rule, the neutral salts; the basic, acid, and double salts, if officinal, are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts refer to these.

Cyanogen, chloric acid, citric acid, malic acid, benzoic acid, succinic acid, and formic acid, are of more common occurrence in combination with a few bases only, and have therefore been omitted from the table. The most frequently occurring compounds of these substances are: cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferricyanide of iron (Prussian blue) III, ferrocyanide of zinc and potassium II—III, chlorate of potassa I, the citrates of the alkalies I, the malates of the alkalies I, malate of sesquioxide of iron I, the benzoates of the alkalies I, the succinates of the alkalies I, and the formates of the alkalies I.

INDEX OF THE SOLUBILITY OF

	KO	NaO	NH_4O	BaO	SrO	CaO	MgO	Al_2O_3	MnO	FeO	Fe_2O_3	CoO	NiO	ZnO
	I	I	I	I	1	I-II	II	II	2	2	II	II	II	II
	I	I	I	I	1	I-II	2		II	II	2	2_{15}	2_{15}	2_{17}
Cl	I	I	I_{12}	I	I	I	1	I	I	I	I_{12}	I	I	1
I	I	1	1	1	1	1	1		1	I	1			1
So_3	I_1	I	I_{13}	III	III	I-III	I	$I_{1\cdot13}$	I	I	I	I	I	I
NO_5	I	I	I	I	I	1	1	1	1	1	1	1	1	1
PO_5	1	I_{10}	1_{10}	2	2	II_{14}	2	2	2	2	II	2	2	2
CO_2	I_2	I_{16}	I	II	II	II	II		II	II		II	2	II
$\bar{O}$	I	I	I	2	2	II	2	2	2	1-2	1-2	2	2	2
BO_3	I_4	I	I	2	2	2	2	2	2	2	2	2	2	2
$\bar{A}$	I	I	I	I	1	I	1	1	1	1	I	1	1	I
$\bar{T}$	$I_{1\cdot3}$	I_7	1_8	2	2	II	1-2	1	1-2	1-2	Is	1	2	2
AsO_5	I	I	1	2	2	2	2	2	2	2	2	2	2	2
AsO_3	I	1	1	2	2	2	2			2	2	2	2	
CrO_3	I	1	1	2	2	2	1	2	1		1		2	1

NOTES.

1. Sulphate of potassa and alumina I.
2. Bicarbonate of potassa I.
3. Binoxalate of potassa I.
4. Tartarized borax (bitartrate of potassa and borate of soda) I.
5. Bitartrate of potassa I-II.
6. Tartrate of potassa and ammonia I.
7. Tartrate of potassa and soda I.
8. Tartrate of potassa and sesquioxide of iron I.
9. Tartrate of antimony and potassa I.
10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Sesquichloride of iron and chloride of ammonium I.
13. Sulphate of alumina and ammonia I.
14. Basic phosphate of lime II.
15. Sulphide of cobalt is pretty readily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.
16. The same applies to sulphide of nickel.

SUBSTANCES IN WATER OR ACIDS.

	CdO	PbO	SnO	SnO_2	BiO_3	CuO	Hg_2O	HgO	AgO	PtO_2	AuO	SbO_3	Cr_2O_3
	2	II_{18}	2	2 & 3	2	II_{22}	II	II	2	2		II_3	II & III
S	2	II	2_{20}	2_{20}	2	2_{23}	II	II	2_{30}	2_{31}		II_{36}	
Cl	1	I-III	I	I	I	I_{24}	II-III	I_{28}	III	$I_{32\text{-}33}$	I_{34}	I_{37}	I & III
I	1	I-II	1	1			II	II	3				
SO_3	I	II-III	1		1	I_{25}	1-2	1_{29}	I-II	1		2	I-II
NO_5	1	I		1	I_{21}	I	I_{27}	I	I	1			I
PO_5	2	2	2			2	2	2	2				2
CO_2	2	II			2	II	2						
O	1	2	2	1	2	2	2	2	2			1-2	1
BO_3	1	2	2		2	2	1						2
Ā	1	I_{19}	1	1	1	I_{26}	1-2	1	1				1
T̄	1-2	2	1-2		2	1		2	2			I_{33}	1
AsO_5		2			2	2	2	2	2			2	2
AsO_3		2				II	2	2	2			2	
CrO_3		II-III	2		2	1	2	1-2	2			2	2

17. Sulphide of zinc is readily soluble in nitric acid, somewhat more sparingly soluble in hydrochloric acid.
18. Minium is converted by hydrochloric acid into chloride of lead; by nitric acid into oxide, which redissolves in an excess of the acid, and into brown binoxide of lead, which is insoluble in nitric acid.
19. Trisacetate of lead I.
20. Proto- and bisulphide of tin are decomposed and dissolved by hydrochloric acid; by nitric acid they are converted into binoxide, which is insoluble in an excess of the acid. Sublimed bisulphide of tin dissolves only in nitrohydrochloric acid.
21. Basic nitrate of teroxide of bismuth II.
22. Ammoniated oxide of copper 1.
23. Sulphide of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.
24. Chloride of copper and ammonium I.
25. Sulphate of copper and ammonia I.
26. Basic acetate of copper, partially soluble in water, and completely in acids.

27. Basic nitrate of suboxide of mercury and ammonia II.
28. Ammonio-chloride of mercury II.
29. Basic sulphate of oxide of mercury II.
30. Sulphide of silver soluble only in nitric acid.
31. Bisulphide of platinum is not affected by hydrochloric acid, and but little by boiling nitric acid; it dissolves in hot nitrohydrochloric acid.
32. Bichloride of platinum and chloride of potassium 1—3.
33. Bichloride of platinum and chloride of ammonium 1—3.
34. Terchloride of gold and chloride of sodium I.
35. Teroxide of antimony is soluble in hydrochloric acid, but not in nitric acid.
36. Tersulphide of antimony and sulphide of calcium I—II.
37. Basic terchloride of antimony II.
38. Tartrate of teroxide of antimony and potassa I.

V.

TABLE OF WEIGHTS AND MEASURES.

GRAMMES.		GRAINS.	DECIGRAMMES.		GRAINS.
1	=	15·4323	1	=	1·5432
2	..	30·8646	2	..	3·0864
3	..	46·2969	3	..	4·6296
4	..	61·7292	4	..	6·1728
5	..	77·1615	5	..	7·7160
6	..	92·5938	6	..	9·2592
7	..	108·0261	7	..	10·8024
8	..	123·4584	8	..	12·3456
9	..	138·8907	9	..	13·8888

CENTIGRAMMES.		GRAINS.	MILLIGRAMMES.		GRAINS.
1	=	·1543	1	=	·0154
2	..	·3086	2	..	·0308
3	..	·4630	3	..	·0463
4	...	·6173	4	..	·0617
5	..	·7717	5	..	·0771
6	..	·9260	6	..	·0926
7	..	1·0804	7	..	·1080
8	..	1·2347	8	..	·1234
9	..	1·3891	9	..	·1389

METRES.		INCHES.	DECIMETRES.		INCHES.
1	=	39·37	1	=	3·937
2	..	78·74	2	..	7·874
3	..	118·11	3	..	11·811
4	..	157·48	4	..	15·748
5	..	196·85	5	..	19·685
6	..	236·22	6	..	23·622
7	..	275·59	7	..	27·559
8	..	314·96	8	..	31·496
9	..	354·33	9	..	35·433

CENTIMETRES.		INCHES.	MILLIMETRES.		INCHES.
1	=	·3937	1	=	·03937
2	..	·7874	2	..	·07874
3	..	1·1811	3	..	·11811
4	..	1·5748	4	..	·15748
5	..	1·9685	5	..	·19685
6	..	2·3622	6	..	·23622
7	..	2·7559	7	..	·27559
8	..	3·1496	8	..	·31496
9	..	3·5433	9	..	·35433

One kilogramme = 15432 grains.
One cubic centimetre = 0·0610 cubic inch.
One litre = 61·0270 cubic inches.

ALPHABETICAL INDEX.

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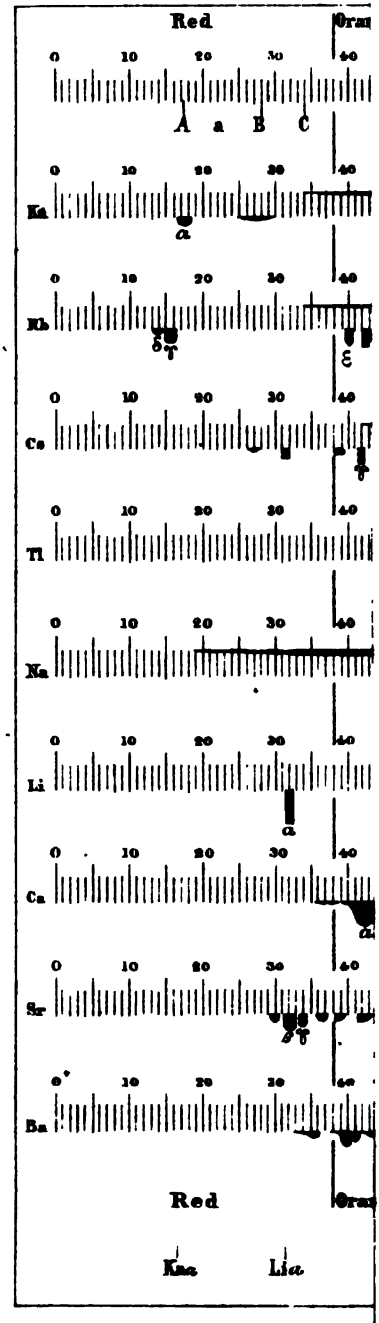
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